Final Draft

IPCC Special Report on Carbon dioxide Capture and Storage

Including the Final Draft Summary for Policymakers for Government Review

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Summary for Policymakers

Juan Carlos Abanades (Spain), Makoto Akai (Japan), Sally Benson (United States), Ken Caldeira (United States), Heleen de Coninck (Netherlands), Peter Cook (Australia), Ogunlade Davidson (Sierra Leone), Richard Doctor (United States), James Dooley (United States), Paul Freund (United Kingdom), John Gale (United Kingdom), Wolfgang Heidug (Germany), Howard Herzog (United States), David Keith (Canada), Marco Mazzotti (Italy and Switzerland), Bert Metz (Netherlands), Leo Meyer (Netherlands), Balgis Osman-Elasha (Sudan), Andrew Palmer (United Kingdom), Riitta Pipatti (Finland), Edward Rubin (United States), Koen Smekens (Belgium), Mohammad Soltanieh (Iran), Kelly (Kailai) Thambimuthu (Australia and Canada)

What is CO_2 capture and storage and how could it contribute to mitigating climate change?

1. CO_2 capture and storage (CCS) is separation of CO_2 from anthropogenic sources, transport to a storage location, and isolation from the atmosphere. CCS would be an option in the portfolio of actions for stabilization of greenhouse gas concentrations while allowing for the continued use of fossil fuels.

   Other mitigation options include energy efficiency improvements, the switch to less carbon intensive fuels, increased use of nuclear power and renewable energy sources, biological sinks, and reduction of non-CO_2 greenhouse gas emissions. CCS has value to mitigation as it may reduce overall mitigation costs and increase flexibility in achieving greenhouse gas emission reductions. The application of CCS would depend on technical maturity, costs, overall potential, regulatory aspects, environmental issues and public perception (Sections 1.1.1, 1.3, 8.3.3.4).

2. The IPCC Third Assessment Report (TAR) indicates that, depending on the assumed baseline emissions and the level of stabilization of greenhouse gas concentrations, over the 21st century, substantial amounts of CO_2 emissions would need to be avoided.

   Most scenarios show that the supply of primary energy will continue to be dominated by fossil fuels until at least the middle of the century. Most model results indicate that known technological[1] options could achieve a broad range of atmospheric CO_2 stabilization levels, such as 550 ppmv, 450 ppmv or below over the next 100 years or more, but implementation would require associated socio-economic and institutional changes. However, no single technology option will provide all of the emissions reductions needed[2] (Sections 1.1, 1.3, 1.6.6).

What are the characteristics of CO_2 capture and storage?

3. Capture of CO_2 can be applied to large point sources, and storage could take place in geological formations or the ocean, in mineral carbonates, or by using the CO_2 in industrial processes.

   Large point sources of CO_2 include large fossil fuel or biomass power generation facilities (including combined production of heat and power), major energy-using industry, synthetic fuel plants and hydrogen facilities. Potential storage methods are: geological storage (in geological formations, such as oil and gas fields, unmineable coal beds and deep, saline water bearing formations), ocean storage (direct release into the ocean water column or onto the deep seafloor) and industrial fixation of CO_2 into inorganic carbonates. This report also discusses industrial uses of CO_2, but this is not expected to contribute much to reduction of CO_2 emissions (see Figure S1) (Sections 1.2, 1.4, 2.2, 2.5.2, Table 2.3).

[1] "Known technological options" refer to technologies that exist in operation or pilot plant stage today, as referenced in the mitigation scenarios discussed in the TAR. It does not include any new technologies that will require profound technological breakthroughs. Known technological options are explained in the TAR and several mitigation scenarios include CCS.

[2] From TAR Summary for Policymakers paragraph 9. This statement refers to technical potential only, and does not take into account the costs. Technical potential as defined in the TAR is the amount by which it is possible to reduce greenhouse gas emissions by implementing a technology or practice that already has been demonstrated.

Figure S.1. Schematic diagram of possible CCS systems. It shows the sources for which CCS might be relevant, transport of CO_2, and storage options.

4. The net reduction of emissions to the atmosphere through CCS is influenced by the fraction of CO_2 captured, the loss in overall efficiency of power plants or industrial processes due to the additional energy required for capture, transport and storage, and the fraction of CO_2 retained in storage over the long term.

Available technology captures about 85 - 95 % of the CO_2 processed in a capture plant. The CCS system needs roughly 10 - 40% more energy than the equivalent plant without CCS, most of it for capture and compression. Due to the associated CO_2 emissions, a total of approximately 80 - 90% of the emissions of the plant without CCS can be avoided (see Figure S2). For storage in mineral carbonates[3] the additional energy requirement is another 30 to 50%. In case of leakage from storage reservoirs, the fraction retained is defined as the fraction of the original amount of injected CO_2 that is still stored at a given time (Sections 1.4.4, 1.5.1, 1.6.3, 7.2, Table 3.15).

[3] Storage of CO_2 in mineral carbonates does not cover ocean storage with enhanced carbonate neutralization as discussed in Chapter 6.

Figure S.2. CO_2 capture and storage from power plants. The loss in conversion efficiency in the capture plant and the additional energy required for transportation and storage result in a larger amount of "CO_2 produced per unit of product" (lower bar) relative to the reference plant (upper bar) without capture (Figure 8.2).

What is the current status of CCS technology?

5. Components of CCS are in various stages of development (see Table SPM.1). Overall, complete CCS systems can be put together from existing technologies that are mature or economically feasible under specific conditions, although the maturity of the overall system may be less than some of its components. Currently, three large-scale[4] CCS systems are in place (Section 1.4.1, 3.3.2, 3.5.2, 4.2.2, Box 5.1, 5.2, 5.3)

[4] Large-scale in this context is defined as at least 1 Mtpa CO_2.

Table S.1. Current maturity of CCS system components. The 'X's indicate the highest level of maturity for each component. For most components, less mature technologies also exist.

CCS component	CCS technology	Research phase[a]	Demonstration phase[b]	Economically feasible under specific conditions[c]	Mature market[d]
Capture	Post combustion			X	
	Pre combustion			X	
	Oxyfuel combustion		X		
	Industrial separation (natural gas processing, ammonia production)				X
Transportation	Pipeline				X
	Shipping			X	
Geological storage	Enhanced Oil Recovery (EOR)[5]				X[6]
	Gas or oil fields			X	
	Saline formations			X	
	Enhanced Coal Bed Methane recovery (ECBM)[7]		X		
Ocean storage	Direct injection	X			
	Carbonate neutralization	X			
Mineral carbonation	Natural silicate minerals	X			
	Waste materials		X		
Industrial uses of CO_2					X

[a] Research phase means that the basic science is understood, but the technology is currently in the stage of conceptual design or testing at the laboratory or bench scale, and has not been demonstrated in a pilot plant.

[b] Demonstration phase means that the technology has been built and operated at the scale of a pilot plant, but further development is required before the technology is ready for the design and construction of a full-scale system.

[c] Economically feasible under specific conditions means that the technology is well understood and used in selected commercial applications, for instance in case of a favourable tax regime or a niche market, processing on the order of 0.1 Mt CO_2/yr , with few (less than 5) replications of the technology.

[d] Mature market means that the technology is now in operation with multiple (5 or more) replications of the technology worldwide.

6. There are different types of CO_2 capture systems: post-combustion, pre-combustion and oxyfuel combustion (Figure S3). The concentration of CO_2, the pressure in the gas flow and the fuel type (solid or gas) are important factors in selecting the capture system.

   Post-combustion capture of CO_2 in power plants is economically feasible under specific circumstances; it is used to capture CO_2 from part of the flue gases from a number of existing power plants. Separation of CO_2 in the natural gas processing industry, which uses basically the same technology, operates in a mature market. The technology required for pre-combustion capture is

[5] For the purposes of this report, EOR means CO_2-driven Enhanced Oil Recovery.

[6] EOR is a mature market technology, but if applied as a climate change mitigation option, it is economically feasible under specific conditions.

[7] ECBM is the use of CO_2 to enhance the recovery of the methane present in unminable coal beds through the preferential adsorption of CO_2 on coal.

widely applied in fertilizer manufacturing and in hydrogen production. Although the initial fuel conversion steps of pre-combustion are more elaborate and costly, there are favourable concentrations of CO_2, and the higher pressures make the separation more efficient. Oxyfuel combustion is in the demonstration phase and uses high purity oxygen. This results in high CO_2 concentrations, but also in increased energy requirements (Sections 3.3, 3.4, 3.5).

Figure S.3. Schematic representation of capture systems. Fuels and products are indicated for oxy-fuel combustion, pre-combustion (including hydrogen and fertilizer production), post-combustion and industrial sources of CO_2 (including natural gas processing facilities, steel and cement production).

7. Pipelines are preferred for transporting large amounts of CO_2 for distances up to around 1,000 km. For smaller amounts or larger distances overseas, use of ships, where applicable, to transport CO_2 is economically more attractive.

In most gas pipelines, compressors at the upstream end drive the flow, but some pipelines have intermediate compressor stations. Moisture is removed from the CO_2 stream to prevent corrosion and to avoid the costs of constructing pipelines of corrosion-resistant material. Pipeline transport of CO_2 operates as a mature market technology (in the US over 2,500 km of pipeline transports more than 40 MtCO_2 per year). Shipping of CO_2, analogous to shipping of liquefied petroleum gases, is economically feasible, but is currently done on a small scale due to limited demand (Sections 4.2.1, 4.2.2, 4.3.2, 4.3.3).

Figure S.4. Overview of geological storage options (Figure 5.3)

8. Storage of CO_2 in deep geological formations (oil and gas fields, saline formations, unminable coal beds) uses many of the same technologies that have been developed by the oil and gas industry and has been proven to be economically feasible under specific conditions for oil and gas fields and saline formations, but not yet for storage in unminable coal beds (see Figure S4)

   Once injected into stable saline formations, or oil or gas fields at depths below 800 m, various physical and geochemical trapping mechanisms would prevent the CO_2 from migrating upwards. A very important physical trapping mechanism is the presence of a caprock.[9] Coal bed storage may take place at shallow depths and relies on the adsorption of CO_2 onto the coal. Its feasibility depends on the permeability of the coal. The combination of CO_2 storage with EOR or ECBM could be attractive because of the additional revenues. Well drilling technology, injection technology, computer simulation of storage reservoir performance, and monitoring methods are being adapted from existing applications to design and operate geological storage projects.

   Three industrial-scale storage projects are in operation: the Sleipner project in a saline aquifer in Norway, the Weyburn EOR project in Canada, and the Salah project in a gas field in Algeria. Others are planned.
   (Sections 5.1.2, 5.6, Boxes 5.1, 5.2, 5.3, 5.4, 5.5).

9. Ocean storage could be done in two ways: by injecting CO_2 into the water column (typically below 1,000 meters) via a fixed pipeline or a moving ship, or by depositing it via a fixed pipeline or an offshore platform on the sea floor at depths below 3,000 m, where the CO_2 is denser

[9] Rock of very low permeability that acts as an upper seal to prevent fluid flow out of a reservoir.

than water and is expected to form a "lake" that would delay dissolution of CO_2 into the surrounding environment (see Figure SPM.5). Ocean storage is still in the research phase.

The transport method is determined by the injection technique used. The dissolved and dispersed CO_2 would become part of the global carbon cycle. In laboratory and small-scale ocean experiments and model simulations, the technologies and associated physical and chemical phenomena, notably changes in acidity (pH), have been studied for a range of ocean storage options (Sections 6.1, 6.2.1.2, 6.5).

Figure SPM.5 Overview of ocean storage options

10. The reaction of CO_2 with metal oxides, which are available widely in silicate minerals and in small quantities in waste streams, would produce stable carbonates. The technology is currently in the research stage, but certain applications in using waste streams are in the demonstration phase.

The natural reaction is very slow, and has to be enhanced by pre-treatment of the minerals, which at present is very energy intensive (7.2.1, 7.2.4, Box 7.1).

11. Industrial uses of captured CO_2 as gas or liquid, or as a feedstock in chemical processes that produce valuable carbon-containing products are possible, but cannot contribute to abatement of CO_2 emissions to a quantitatively significant extent.

The potential for industrial uses of CO_2 is small, the CO_2 is generally retained over short periods (usually months or years), and a process using captured CO_2 as feedstock instead of fossil hydrocarbons, could also lead to increased CO_2 emissions (7.3.1, 7.3.2, 7.3.3, 7.3.4).

What are the sources of CO_2 and where are they located?

12. Large point sources of CO_2 are concentrated in major industrial areas, mostly in industrialized countries, but also in developing countries. CO_2 sources are often close (< 300 km) to areas that potentially hold reservoirs for geological storage (see Figure SPM.6), but only a small proportion of large emission sources might be close to ocean storage locations.

Most of the future increase in the number of sources is expected to take place in developing countries, but the location and proximity to storage sites are uncertain. Scenarios indicate that, by 2050 and given technical limitations, around 20 - 40% of global fossil fuel CO_2 emissions could be amenable to capture (Sections 2.3, 2.4.3).

13. In the longer term, CCS enables low-carbon production of electricity or hydrogen that could eliminate small CO_2 sources from transport and distributed energy supply systems. This would lead to additional large point sources of CO_2.

Electricity could be used in electric vehicles, and hydrogen could be used in fuel cells, for instance in the transport sector. Gas and coal based reforming with integrated CO_2 separation (without storage) is currently the dominant option for production of hydrogen. More hydrogen or electricity production would result in an increased number of large CO_2 sources amenable to capture and storage. At present, it is difficult to project the likely number, location and size of such sources (Sections 2.5.1, 2.5.1.2).

Figure S.6. Geographical relationship between CO_2 emission sources and sedimentary basins with geological storage potential. The dots indicate CO_2 emission sources of 0.1 – 50 $MtCO_2/yr$. Prospectivity is a qualitative assessment of the likelihood that a suitable storage location is present in a given area based on the available information. Being only a perception it will change over time and with new information (Figure 2.5).

What are the costs for CCS and what is the economic potential?

14. When applying CCS to electricity production under current conditions, costs are estimated to increase by about 0.01 - 0.05 US$/kWh[10,11], depending on the fuel, the specific technology, and the national circumstances. Including the benefits of EOR would reduce additional electricity production costs due to CCS by around 0.01 to 0.02 US$/kWh[12] (see Table S2 and for costs in US$/tCO$_2$ avoided, see Table S3). Using biomass would add substantially to the electricity costs, particularly due to the current small scale of the plants.

    In the future, the costs of CCS could be reduced by technological development and economies of scale. Increases in fuel prices would tend to make operation more expensive, and costs vary considerably in both absolute and relative terms from country to country. Economies of scale could bring down the cost of biomass-based CCS systems considerably over time. When applying CCS to biomass-fuelled or co-fired electricity plants, this would lead to lower or negative CO$_2$ emissions[13], which partly compensates for the additional costs for this option, depending on the value of CO$_2$ emission reductions (Sections 3.7.5.4, 8.2.4, Table 8.3).

15. Retrofitting existing plants with CCS normally leads to higher costs than for newly built power plants with capture, except in relatively new and highly efficient plants and cases where a plant is upgraded or substantially rebuilt.

    Costs of retrofitting CCS to existing installations vary. Industrial sources of CO$_2$ can more easily be retrofitted with CO$_2$ separation, but integrated systems would need more profound adjustment. In order to limit future retrofit costs, new plant designs could take future CCS application into account (3.1.4, 3.2.3, 3.2.4).

Table S.2. Costs of CCS: production costs of electricity for different types of generation, without capture and for the CCS systems as a whole. The cost of a full CCS system for electricity generation from a newly built, full-scale fossil fuel-based power plant depends on a number of factors, including the characteristics of the power plant and the capture system, the specifics of the storage site, the amount of CO$_2$, and the required transport distance. The numbers assume experience with a full-scale plant. EOR benefits are based on oil prices of 15 - 20 US$ per barrel. Gas prices are assumed to be 2.8 - 4.4 US$/GJ, coal prices 1 - 1.5 US$/GJ (based on Table 8.3 and 8.4).

	NGCC[a] (US$/kWh)	PC[b] (US$/kWh)	IGCC[c] (US$/kWh)
Without capture	0.03 - 0.05	0.04 - 0.05	0.04 - 0.06
Power plant with capture and geological storage	0.04 - 0.08	0.06 - 0.10	0.05 - 0.09
Power plant with capture and EOR[11]	0.04 - 0.07	0.05 - 0.08	0.04 - 0.07

[a] Natural Gas Combined Cycle
[b] Pulverized Coal
[c] Integrated Gasification Combined Cycle

[10] All costs in this report are expressed in 2002 US$.
[11] Numbers refer to electricity generation costs, not electricity prices.
[12] Based on oil prices of 15 - 20 US$ per barrel
[13] Provided the biomass is sustainably grown

Table S.3 CO_2 avoidance costs for the CCS system for electricity generation, for different combinations of reference power plants and power plants with capture, transport and storage (geological and EOR[14]). EOR benefits are based on oil prices of 15 - 20 US$ per barrel. Gas prices are assumed to be 2.8 - 4.4 $/GJ, coal prices 1 - 1.5 $/GJ (based on Table 8.3a).

	NGCC reference plant	PC reference plant
	US$/tCO$_2$ avoided	US$/tCO$_2$ avoided
Power plant with capture and geological storage		
NGCC	40 – 90	20 – 60
PC	70 – 270	30 – 70
IGCC	40 – 220	20 – 70
Power plant with capture and EOR[11]		
NGCC	20 – 70	0 – 30
PC	50 – 240	10 – 40
IGCC	20 – 190	0 – 40

16. In most CCS systems, the cost of capture (including compression) is the largest cost component.

    Costs for the various components of a CCS system vary widely, depending on the base case and the wide range in source, transport and storage situations (see Table S4). Over the next decade the cost of capture could be reduced by 20-30% and more can be achieved by new technologies that are still in the research or demonstration phase. The costs of transport and storage of CO_2 could decrease slowly as the technology matures further and the scale increases (Sections 1.5.1.4, 3.7.13, 8.2).

17. Energy and economic models indicate that the major CCS system's contribution to climate change mitigation would come from deployment in the electricity sector. For this to happen, the price of carbon dioxide emission reductions would have to exceed 25 - 30 US$/tCO$_2$ over the lifetime of the CCS project, or an equivalent limit on CO_2 emissions would have to be mandated.

    Low-cost capture possibilities in combination with short (< 50 km) transport distances and storage options that generate revenues (such as EOR) can lead to storage of CO_2 (up to 360 MtCO$_2$ cumulatively) under circumstances of low or absent incentives (Sections 2.2.1.3, 2.3.2, 2.4, 8.3.3)

[14] IGCC is not included as a reference power plant that would be built today since this technology is not yet widely deployed in the electricity sector and is usually slightly more costly than a PC plant. The incremental cost in US$/tCO2 avoided for an IGCC plant when CCS is applied would range from 15 to 55 US$/tCO$_2$ avoided with geological storage, and -5 to 30 US$/tCO$_2$ avoided with EOR.

Table S.4 Current cost ranges for the components of a CCS system, applied to a given type of power plant or industrial source. The costs of the separate components cannot simply be summed to calculate the costs of the whole CCS system in US$/$CO_2$ avoided. All numbers are representative of costs for full-scale, new power plants with natural gas prices assumed to be 2.8 - 4.4 US$/GJ and coal prices 1 - 1.5 US$/GJ (8.2.1, 8.2.2, 8.2.3, Table 8.1 and 8.2).

Cost component	Cost range	Remarks
Capture from a coal- or gas-fired power plant	15 - 75 US$/$tCO_2$ net captured	Includes net costs of captured CO_2 for plants with capture, compared to the same plant without capture
Capture from ammonia production or gas processing	5 - 25 US$/$tCO_2$ net captured	
Capture from other industrial sources	25 - 115 US$/$tCO_2$ net captured	
Transportation	1 - 8 US$/$tCO_2$ transported	Per 250 km pipeline or shipping for mass flow rates of 5 (high end) to 40 (low end) MtCO_2/yr.
Geological storage	0.5 - 8 US$/$tCO_2$ injected	Excluding potential revenues from EOR or ECBM.
Ocean storage	5 - 30 US$/$tCO_2$ injected	Including offshore transportation of 100 - 500 km
Geological storage: monitoring and verification	0.1 - 0.3 US$/$tCO_2$ injected	Depend on the regulatory requirements
Mineral carbonation	50 - 100 US$/$tCO_2$ net mineralized	Range for the best case studied. Includes additional energy use for carbonation

18. Available evidence suggests that worldwide, it is likely[15] that there is 2,000 GtCO_2 (545 GtC) of storage capacity in geological formations. Uncertain estimates of upper limits of the technical potential of geological storage, ocean storage and mineral carbonation are on the order of thousands of GtCO_2.

The technical potential for geological storage primarily consists of oil and gas reservoirs, and saline formations. The current upper limit estimates for saline formations are uncertain due to lack of information and an agreed methodology, whereas oil and gas reservoirs are better characterized. Technical storage potential in the oceans could be up to thousands of GtCO_2, depending on the assumed stabilization level in the atmosphere[16], and depending on environmental factors such as ocean pH change. Mineral carbonation could have a similar potential, depending on the fraction of silicate reserves that can be technically exploited, and environmental issues such as the volume of product disposal (Sections 5.3, 6.3, 7.2.8.2, Table 5.2).

19. In most scenarios for stabilization of atmospheric greenhouse gas concentrations between 450 and 750 ppmv CO_2 and in a least-cost portfolio of mitigation options, the economic potential[17] of CCS would amount to 220 - 2,200 GtCO_2 (60 - 600 GtC), which would mean that CCS contributes 15 to 55% to the cumulative mitigation effort worldwide until 2100, averaged over a range of baseline scenarios (see Figure S.7). It is likely[18] that the technical potential for geological storage is sufficient to cover the high end of the economic potential range.

[15] "Likely" is a probability between 66 and 90%.

[16] This approach takes into account that the CO_2 injected in the ocean will after some time reach equilibrium with the atmosphere.

[17] Economic potential is the amount of greenhouse gas emissions reductions from a specific option that would make sense economically, given prevailing circumstances (i.e. a price of CO_2 reductions and costs of other options)

[18] "Very likely" is a probability of 90 to 99%

Uncertainties in these economic potential estimates are significant. For CCS to achieve such an economic potential, several hundreds to thousands of CO_2 capture systems would need to be installed over the coming century, each capturing some 1 - 5 $MtCO_2$ per year. The actual use of CCS, as for other mitigation options, may be lower than the economic potential due to barriers such as environmental impacts, risks of leakage, and the lack of a clear legal framework or public acceptance (Sections 1.4.4, 8.3.1, 8.3.3, 8.3.3.4).

20. In most scenario studies, the role of CCS in mitigation portfolios increases over the course of the century (see Figure SPM.7) and including CCS in a mitigation portfolio reduces the costs of stabilizing CO_2 concentrations by 30% or more.

One aspect of the cost competitiveness of CCS systems is that CCS technologies are applicable with most current energy infrastructures (Sections 1.5, 8.3.3.4, Box 8.3).

What are the local health, safety and environment risks of CCS?

21. The local risks[19] associated with CO_2 transport could be similar to or lower than those posed by comparable operations.

For existing CO_2 pipelines, mostly in areas of low population density, accident rates reported per kilometre pipeline are very low and are comparable to those for hydrocarbon pipelines, and the impacts would probably not be more severe than those with natural gas accidents. If a sudden and brief large release of CO_2 occurred, the local impacts on health could be significant; a concentration of CO_2 greater than 7 - 10% in air would cause immediate dangers to human life and health (Sections 4.5.2, A.4.1).

[19] In discussing the risks, we assume that risk is the product of the probability that an event will occur and the consequences of the event if it does occur.

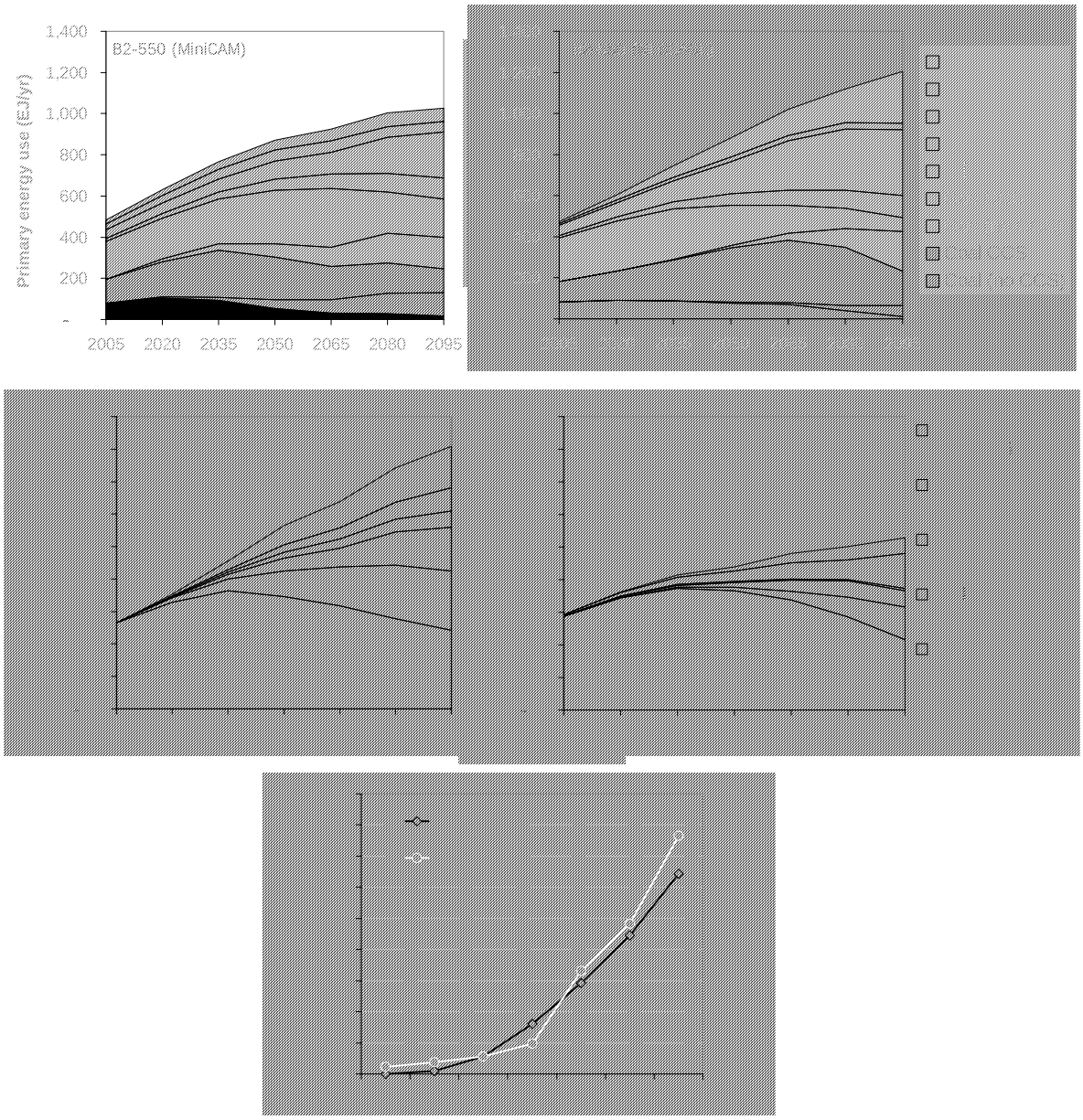

Figure S.7. Illustration of the possible economic potential for CCS, for two scenario studies for a 550 ppmv CO_2 stabilization case. a) and b) are the possible contributions of energy supply options to the primary energy mix, highlighting that the energy use can differ with varying assumptions. c) and d) represent the contributions of CCS and other mitigation options to a portfolio for stabilization at 550 ppm CO_2, using an IPCC-SRES B2 baseline[20] for two model calculations ; e) the marginal cost for CO_2 reduction (US$/t$CO_2$ avoided) over time for the two scenario runs (8.3.3, Figure 8.4, Box 8.3)

22. Risks posed by geological storage would depend on the criteria and available subsurface information used for site selection, the design of the monitoring program to detect problems, the regulatory system, and the appropriate use of remediation methods to stop or control CO_2 releases if they arise.

Natural CO_2 reservoirs contribute to the understanding of the behaviour of CO_2 underground. Features of storage sites with a low probability of leakage include highly impermeable caprocks, absence of leakage paths and effective trapping mechanisms. There are two different

[20] The different baseline emissions in the two panels represent the highest and lowest projections of the B2 scenario family (see figure 8.3). See chapter 8.3.1.2 for explanation of this particular SRES scenario.

Technical Summary

Coordinating Lead Authors
EDWARD RUBIN (UNITED STATES), LEO MEYER (NETHERLANDS), HELEEN DE CONINCK (NETHERLANDS)

Lead Authors
Juan Carlos Abanades (Spain), Makoto Akai (Japan), Sally Benson (United States), Ken Caldeira (United States), Peter Cook (Australia), Ogunlade Davidson (Sierra Leone), Richard Doctor (United States), James Dooley (United States), Paul Freund (United Kingdom), John Gale (United Kingdom), Wolfgang Heidug (Germany), Howard Herzog (United States), David Keith (Canada), Marco Mazzotti (Italy and Switzerland), Bert Metz (Netherlands), Balgis Osman-Elasha (Sudan), Andrew Palmer (United Kingdom), Riitta Pipatti (Finland), Koen Smekens (Belgium), Mohammad Soltanieh (Iran), Kelly (Kailai) Thambimuthu (Australia and Canada), Bob van der Zwaan (Netherlands).

Review Editor
Ismail El Gizouli (Sudan)

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1. Introduction and framework of this report

Carbon dioxide capture and storage (CCS), the subject of this Special Report, is one of the options for reducing atmospheric emissions of CO_2 from human activities. The purpose of this Special Report is to assess the current state of knowledge regarding the technical, scientific, environmental, economic and societal dimensions of CCS and put CCS in context of other options in the portfolio of potential climate change mitigation measures.

The organization of this Technical Summary follows the structure of the Special Report. This introductory section presented the general framework for the assessment together with a brief overview of CCS systems. Section 2 next characterizes the major sources of CO_2, which is needed to assess the feasibility of CCS on a global scale. Technological options for CO_2 capture are then discussed in Section 3, while Section 4 focuses on methods of CO_2 transport. Each of the storage options is then addressed. Section 5 focuses on geological storage, Section 6 on ocean storage, and Section 7 on mineral carbonation and industrial uses of CO_2. The overall costs and economic potential of CCS are then discussed in Section 8, followed by an examination in Section 9 of the implications of CCS for greenhouse gas emissions inventories and accounting. The Technical Summary concludes with a discussion of gaps in knowledge, especially those critical for policy considerations.

Overview of CO_2 capture and storage

CO_2 is emitted principally from the burning of fossil fuels, both in large combustion units such as used for electric power generation, as well as from smaller, distributed sources such as automobile engines and furnaces used in residential and commercial buildings. CO_2 emissions also result from some industrial and resource extraction processes, as well as from the burning of forests during land clearance. CCS would most likely be applied to large point sources of CO_2, such as power plants or large industrial processes. Some of these sources could supply decarbonized fuel such as hydrogen to the transportation, industrial and building sectors, and thus reduce emissions from those distributed sources.

CCS involves the use of technology to first collect and concentrate the CO_2 produced in a large-scale process, transport it to a suitable storage location, and then store it away from the atmosphere for a long period of time. Applications of CCS would thus allow fossil fuels to be used with little emissions of greenhouse gases. Application of CCS to biomass energy sources could result in the net removal of CO_2 from the atmosphere (often referred to as "negative emissions") by capturing and storing the atmospheric CO_2 taken up by the biomass, provided the biomass is grown sustainably.

Figure TS.1 illustrates the three main components of the CCS process: capture, transport and storage. All three components are found in industrial operations today although mostly not for the purpose of CO_2 storage. The capture step involves separating CO_2 from other gaseous products. For fuel-burning processes such as power plants, separation technologies can be used to capture CO_2 after combustion or to decarbonize the fuel before combustion. The transport step may be required to carry captured CO_2 to a suitable storage site that may be distant from the CO_2 source. To facilitate both transport and storage, the captured CO_2 gas is typically compressed to a high density at the capture facility. Potential storage methods include injection into underground geological formations, injection into the deep ocean, or industrial fixation into inorganic carbonates. Some industrial processes also might utilize and store small amounts of captured CO_2 in manufactured products.

[1] Synthesis Report, Third Assessment Report, Intergovernmental Panel on Climate Change, Geneva, 2001.

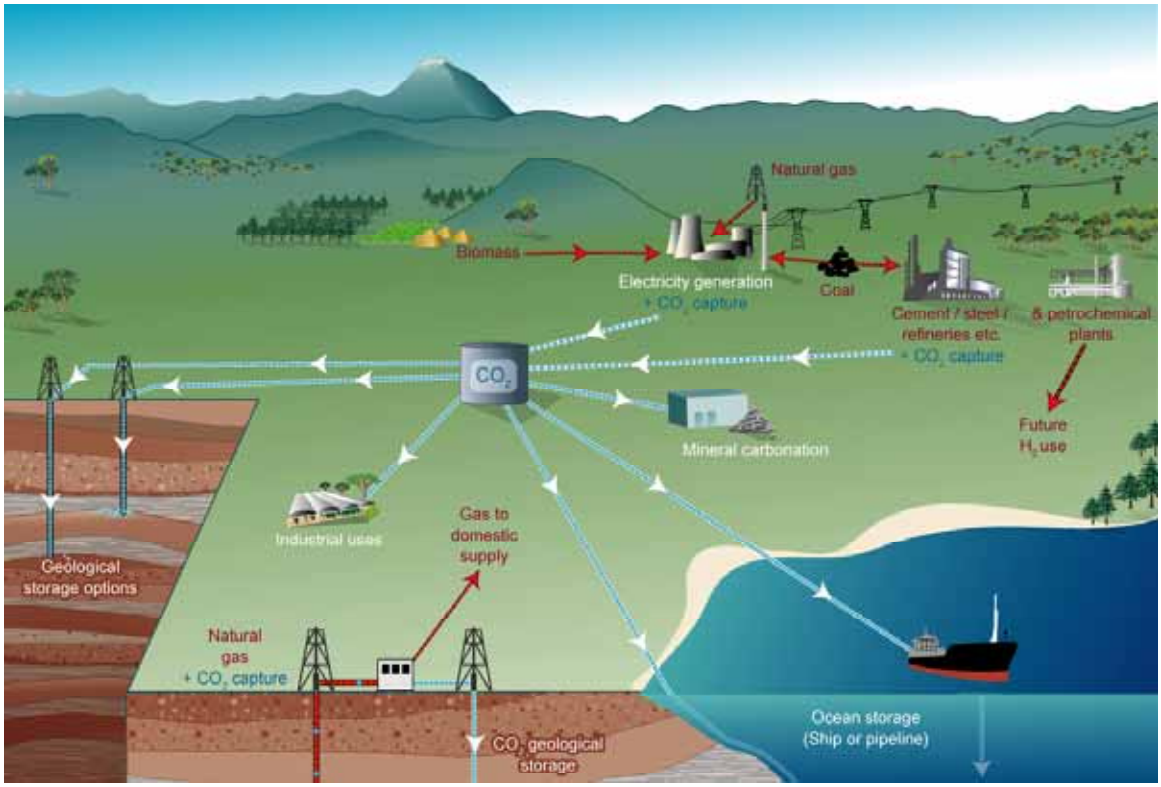


Figure TS.1. Schematic diagram of possible CCS systems. It shows the sources for which CCS might be relevant, transport of CO_2, and storage options (Courtesy CO2CRC).

The technical maturity of specific CCS system components varies greatly. Some technologies are extensively deployed in mature markets, primarily in the oil and gas industry, while others are still in the research, development or demonstration phase. Table TS.1 provides an overview of the current status of all CCS components. As of mid-2005, there have been three commercial projects that link CO_2 capture and geological storage: the offshore Sleipner natural gas processing project in Norway, the Weyburn Enhanced Oil Recovery (EOR)[2] project in Canada (which stores CO_2 captured in the United States) and the In Salah natural gas project in Algeria. Each captures and stores from 1-2 $MtCO_2$ per year. It should be noted, however, that CCS has not yet been applied at a large (e.g., 500 MW) fossil fuel power plant, and that the maturity of the overall system may be less than some of its components.

[2] In this report, EOR means enhanced oil recovery using CO_2.

Table TS.1. Current maturity of CCS system components. The X's indicate the highest level of maturity for each component. For most components, also less mature technologies exist.

CCS component	*CCS technology*	*Research phase*[a]	*Demonstration phase*[b]	*Economically feasible under specific conditions*[c]	*Mature market*[d]
Capture	Post combustion			X	
	Pre combustion			X	
	Oxyfuel combustion		X		
	Industrial separation (natural gas processing, ammonia production)				X
Transport	Pipeline				X
	Ship			X	
Geological storage	Enhanced oil recovery				X[e]
	Gas or oil fields			X	
	Deep saline formations			X	
	Enhanced coal bed methane recovery (ECBM)[f]		X		
Ocean storage	Direct injection	X			
	Carbonate neutralization	X			
Mineral carbonation	Natural silicate minerals	X			
	Waste materials		X		
Industrial uses of CO_2					X

[a] Research phase means that the basic science is understood, but the technology is currently in the stage of conceptual design or testing at the laboratory or bench scale, and has not been demonstrated in a pilot plant.

[b] Demonstration phase means that the technology has been built and operated at the scale of a pilot plant, but further development is required before the technology is ready for the design and construction of a full-scale system.

[c] Economically feasible under specific conditions means that the technology is well understood and used in selected commercial applications, for instance in case of a favourable tax regime or a niche market, processing on the order of 0.1 $MtCO_2/yr$, with few (less than 5) replications of the technology.

[d] Mature market means that the technology is now in operation with multiple (5 or more) replications of the technology worldwide.

[e] EOR is a mature market, but is in the demonstration phase as a climate change mitigation option.

[f] ECBM is the use of CO_2 to enhance the recovery of the methane present in unminable coal beds through the preferential adsorption of CO_2 on coal.

Why the interest in CO_2 capture and storage?

In 1992, international concern about climate change led to the United Nations Framework Convention on Climate Change (UNFCCC). The ultimate objective of that Convention is to achieve stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. From this perspective, the context for considering CCS (and other mitigation options) is that of a world constrained in CO_2 emissions, consistent with the international goal of stabilizing atmospheric greenhouse gas concentrations.

Most scenarios of future global energy use project a substantial increase of CO_2 emissions throughout this century in the absence of specific actions to mitigate climate change and suggest

that the supply of primary energy will continue to be dominated by fossil fuels until at least the middle of the century (see Section 8). The magnitude of the emissions reduction needed to stabilize the atmospheric concentration of CO_2 will depend on both the level of future emissions (the baseline), and the desired target for long-term CO_2 concentration: the lower the stabilization target and the higher the baseline emissions, the larger the required reduction in CO_2 emissions. According to IPCC's Third Assessment Report (TAR), to stabilize the CO_2 concentration at 450 to 750 ppmv[3], cumulative emissions of hundreds or even thousands of gigatonnes of CO_2 would need to be prevented during this century, depending on the scenario considered. The TAR also found that, "most model results indicate that known technological options[4] could achieve a broad range of atmospheric CO_2 stabilization levels, such as 550 ppmv, 450 ppmv or below over the next 100 years or more", but that "no single technology option will provide all of the emissions reductions needed". Rather, a combination of mitigation measures will be needed to achieve stabilization. These known technological options are available for stabilization, although the IPCC TAR cautions that, "implementation would require associated socio-economic and institutional changes".

In this context, the availability of CCS in the portfolio of options for reducing greenhouse gas emissions could facilitate achieving stabilization goals. Other technological options, which have been examined more extensively in previous IPCC assessments, include: (1) reducing energy demand by increasing the efficiency of energy conversion and/or utilization devices; (2) decarbonizing energy supplies (either by switching to less carbon intensive fuels (such as from coal to natural gas), and/or by increasing the use of renewable energy sources and/or nuclear energy (each of which, on balance, emit little or no CO_2); (3) sequestering CO_2 through the enhancement of natural sinks by biological fixation; and (4) reducing non-CO_2 greenhouse gases. Model results presented later in this report suggest that use of CCS in conjunction with other measures could significantly reduce the cost of achieving stabilization and would increase flexibility in achieving these reductions, while allowing for the continued use of fossil fuels. The heavy worldwide reliance on fossil fuels today (approximately 80% of global energy use), the potential for CCS to reduce CO_2 emissions over the next century, and the compatibility of CCS systems with current energy infrastructures explain the interest in this technology.

Major issues for this assessment

There are a number of issues that need to be addressed in trying to understand the role that CCS could play in mitigating climate change. Questions that arise, and that are addressed in different sections of this Summary, include the following:

- What is the current status of CCS technology?
- What is the potential for capturing and storing CO_2?
- What are the costs of implementation?
- How long should CO_2 be stored to significantly mitigate climate change?
- What are the health, safety and environmental risks of CCS?
- What can be said about the public perception of CCS?
- What are the legal issues for implementing CO_2 storage?
- What are the implications for emission inventories and accounting?
- What is the potential for diffusion and transfer of CCS technology?

[3] ppmv is parts per million by volume.

[4] "Known technological options" refer to technologies that exist in operation or pilot plant stage today, as referenced in the mitigation scenarios discussed in IPCC's Third Assessment Report. It does not include any new technologies that will require drastic technological breakthroughs. In this way it can be considered to be a conservative estimate, considering the length of the scenario period.

When CCS is analyzed as a climate change mitigation option, it is of central importance that all resulting emissions, especially those of CO_2, in or through the system, are known and can be assessed in a transparant way. The importance of taking a "systems" view of CCS is therefore stressed, as the selection of an appropriate system boundary is essential for proper analysis. Given the energy requirements associated with capture and some storage and utilization options, and the possibility of leaking storage reservoirs, the assessment of the full CCS chain is vital.

From the perspectives of both atmospheric stabilization and long-term sustainable development, storage of CO_2 must extend over timescales long enough to contribute significantly to climate change mitigation. This report expresses the duration of CO_2 storage in terms of the "fraction retained", defined as the fraction of the cumulative mass of CO_2 injected that is retained in a storage reservoir during a specified period of time. Estimates of such fractions for different time periods and storage options are presented later. Questions arise not only about how long CO_2 will remain stored, but also what are acceptable amounts of slow, continuous leakage[5] from storage. Different perspectives on this question are discussed in Section 8.

CCS would be an option for countries that have significant sources of CO_2 suitable for capture, access to storage, and experience with oil or gas operations, and need to satisfy their development aspirations in a carbon-constrained environment. Literature assessed in the IPCC Special Report Methodological and Technological Issues and Technology Transfer indicates that many barriers could inhibit the deployment in developing countries, even of technologies that are mature in industrialized countries. Addressing these barriers and creating conditions that would facilitate diffusion of the technology to developing countries would be a major issue for the adoption of CCS worldwide.

2. Sources of CO_2

This section describes the major current sources of anthropogenic CO_2 emissions and their relation to potential storage sites. As noted earlier, CO_2 emissions from human activity arise from a number of different sources, predominately from the combustion of fossil fuels in the power generation, industrial, buildings and transportation sectors. CO_2 also is emitted from certain industrial processes like cement manufacture or hydrogen production and from the combustion of biomass. Future emissions are also discussed.

Current CO_2 sources and characteristics

To assess the potential of CCS as an option for reducing global CO_2 emissions, the current global geographical relationship between large stationary CO_2 emission sources and their proximity to potential storage sites has been examined. CO_2 emissions in the building and transportation sectors have not been considered in this analysis because these emission sources are small and often mobile and hence are not suitable for capture. Following this, potential future sources of CO_2 based on several scenarios of future global energy use and emissions over the next century are analyzed.

Globally, emissions of CO_2 from fossil fuel use in the year 2000 totalled about 23.5 $GtCO_2$/yr (6 GtC/yr). Of this, close to 60 % was attributed to large (>0.1 $MtCO_2$/yr) stationary emission sources (See Table TS.2).Not all of these sources are amenable to capture of CO_2, however. Although the sources evaluated are distributed throughout the world, the database reveals four particular clusters of emissions: North America (mid-west and eastern USA), Europe (north western region), East Asia

[5] In respect of storage of CO_2, leakage is defined as the escape of injected fluid from storage, which is the most common meaning used in this Summary. If used in the context of trading of carbon dioxide emission reductions, it may signify, the change of anthropogenic emissions by sources or removals by sinks which occurs outside the project boundary.

(eastern coast of China) and South Asia (Indian subcontinent). By contrast large-scale biomass sources are much smaller in number and less globally distributed.

Table TS.2. Profile by process or industrial activity of worldwide large stationary CO_2 sources with emissions of more than 0.1 $MtCO_2$ per year.

Process	No. of sources	Emissions ($MtCO_2$/yr)
Fossil Fuels		
Power (coal, gas, oil and others)	4,942	10,539
Cement production	1,175	932
Refineries	638	798
Iron and steel industry	269	646
Petrochemical industry	470	379
Oil and gas processing	N/A	50
Other sources	90	33
Biomass		
Bioethanol and bioenergy	303	91
Total	**7,887**	**13,466**

Currently, the vast majority of large emission sources have CO_2 concentrations of less than 15% (in some cases, substantially less). However, a small portion (less than 2%) of the fossil fuel based industrial sources has CO_2 concentrations greater than 95%. The sources with high concentration are potentially suitable for early implementation of CCS because only dehydration and compression would be required at the capture stage (see Section 3). An analysis of the high purity sources that are within 50 km of storage formations that have the potential to generate revenues (via the use of CO_2 for ECBM or EOR) indicates that such sources currently emit approximately 360 Mt CO_2 per year. Some biomass sources like bioethanol production also generate high concentration CO_2 sources which could also be used in similar applications.

The distance between emission location and storage site can have a significant bearing on whether or not CCS can play a significant role in reducing CO_2 emissions. Figure TS.2 depicts the geographical relationship between major CO_2 emission sources (indicated by dots) and sedimentary basins which might have geological storage potential (shown in different shades of grey). Globally, this indicates that there is potentially good correlation between major sources and prospective sedimentary basins, with many sources lying either directly above, or within a reasonable distance (less than 300 km) from an area with potential for geological storage. The basins indicated in Figure TS.2 have not been identified or evaluated as suitable storage reservoirs; more detailed geological analysison a regional level is required to confirm the suitability of these potential storage sites.

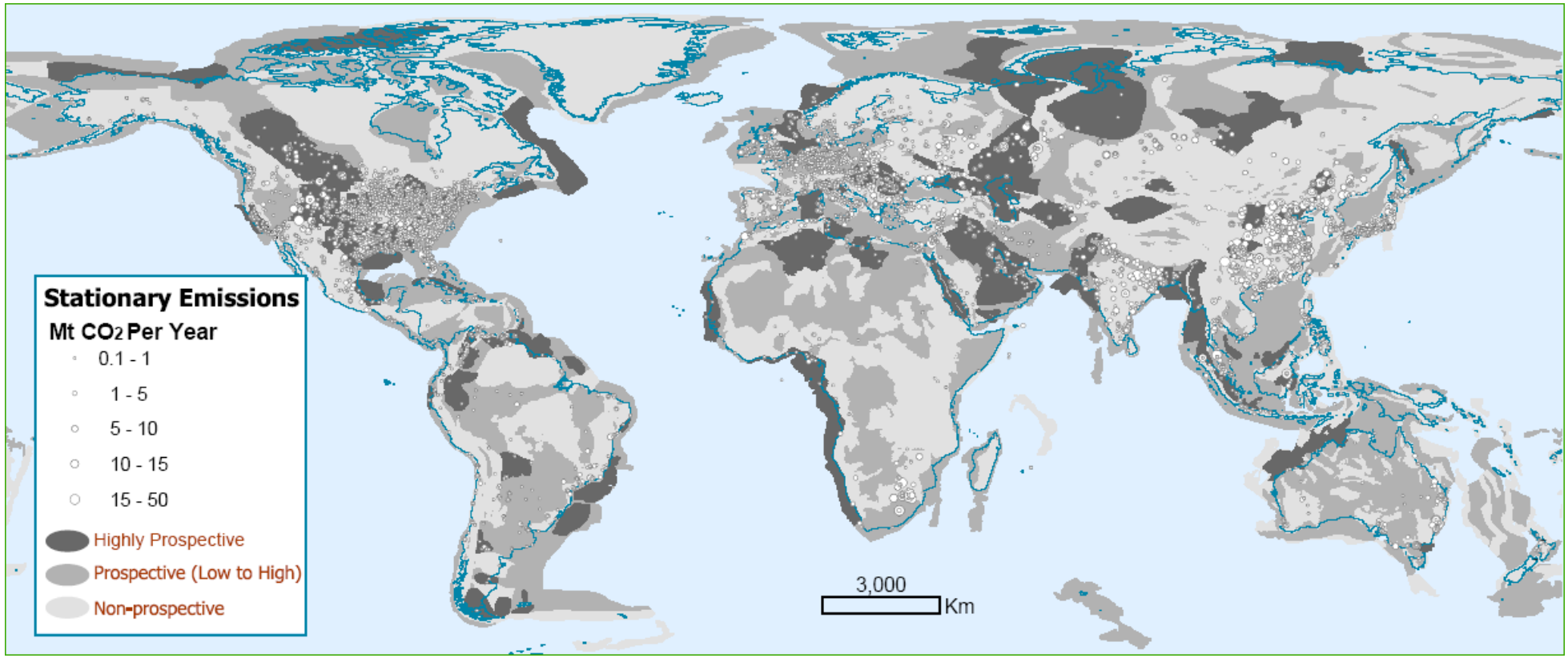


Figure TS.2. Geographical relationship between CO_2 emission sources and sedimentary basins with geological storage potential. The dots indicate CO_2 emission sources of 0.1 – 50 $MtCO_2/yr$. Prospectivity is a qualitative assessment of the likelihood that a suitable storage location is present in a given area based on the available information. Being only a perception it will change over time and with new information (Courtesy Geoscience Australia).

Future emission sources

In the IPCC Special Report on Emission Scenarios (SRES), the future emissions of CO_2 are projected based on six illustrative scenarios in which global CO_2 emissions range from 29 to 44 $GtCO_2$ per year in 2020 (8 - 12 GtC), and from 23 to 84 $GtCO_2$ per year in 2050 (6 - 23 GtC). Up to 2050, it is projected that the number of CO_2 emission sources from the electric power and industrial sectors will increase significantly, predominantly in South and East Asia. In contrast, the number of such sources in Europe may decrease slightly. The proportion of sources with high and low CO_2 content will be a function of the size and rate of introduction of plants employing gasification or liquefaction of fossil fuels to produce hydrogen, or liquid and gaseous products. The more such plants, the greater number of sources with high CO_2 concentration amenable to capture.

The projected potential of CO_2 capture associated with the above emission ranges has been estimated at an annual 2.6 to 4.9 $GtCO_2$ by 2020 (0.7 - 1.3 GtC) and 4.7 to 37.5 $GtCO_2$ by 2050 (1.3 - 10 GtC). These numbers correspond 9 - 12%, and 21 - 45% of the global CO_2 emissions in 2020 and 2050, respectively. The emission and capture ranges reflect the inherent uncertainties of scenario and modelling analyses and technical and economic limitations of applying CCS. The scenarios only take CO_2 capture from fossil fuels into account, not from biomass sources.

Relevant to the future number and size of large, stationary CO_2 sources with high concentrations is the potential development of low-carbon energy carriers. Scenarios also suggest that within several decades, large scale production of low-carbon energy carriers such as electricity or hydrogen could begin displacing the fossil fuels currently used by small, distributed sources in the buildings and transportation sectors (see Section 8). These energy carriers could be produced from fossil fuels and/or biomass in large plants that would generate large point sources of CO_2 (power plants or plants similar to current plants producing hydrogen from natural gas). These sources would be amenable to CO_2 capture. Such applications of CCS could eliminate small transport and distributed energy supply system CO_2 emissions . At present, however, it is difficult to project the likely number, size, or geographical distribution of such additional sources associated with such developments.

3. Capture of CO_2

This chapter examines the capture technology component of the CCS system. As shown in Section 2, electric power plants and other large scale industrial processes are the primary candidates for capture and the main focus of this chapter.

Capture technology options and applications

The purpose of CO_2 capture is to produce a concentrated stream of CO_2 at high pressure that can readily be transported to a storage site. Although, in principle, the entire gas stream containing low concentrations of CO_2 could be transported and injected underground, the energy and other costs of doing so generally make this approach impractical. Therefore, it is necessary to produce a nearly pure CO_2 stream for transport and storage. Applications separating CO_2 in large industrial plants, including natural gas treatment plants and ammonia production facilities, are already in operation today. Currently, the CO_2 typically is removed to purify other industrial gas streams. Only in a few cases has it been used for storage purposes; in most cases it is emitted to the atmosphere. Capture processes also have been used to obtain commercially useful amounts of CO_2 from flue gas streams generated by the combustion of coal or natural gas. To date, however there have been no applications of CO_2 capture at large (e.g., 500 MW) fossil fuel power plants.

Depending on the process or power plant application of interest, there are three main approaches to capturing the CO_2 generated from a primary fossil fuel (coal, natural gas or oil), biomass, or mixtures of these fuels:

Post-combustion systems separate CO_2 from the flue gases produced by the combustion of the primary fuel in air. These systems normally use a liquid solvent to capture the small fraction of CO_2 (typically 3–15% by volume) present in a flue gas stream whose main constituent is nitrogen (from air). For a modern pulverized coal (PC) power plant or a natural gas combined cycle (NGCC) power plant, current post-combustion capture systems would typically employ an organic solvent such as monoethanolamine (MEA).

Pre-combustion systems process the primary fuel in a reactor with steam and air or oxygen to produce a mixture of mainly carbon monoxide and hydrogen (commonly called synthesis gas). Additional hydrogen, together with CO_2, is produced by reacting the carbon monoxide with steam in a second reactor (called a shift reactor). The resulting mixture of hydrogen and CO_2 can then be separated into a gas stream of CO_2, and a stream of hydrogen. If the CO_2 is stored, the hydrogen is a carbon-free energy carrier that can be combusted to generate power and/or heat. Although the initial fuel conversion steps are more elaborate and costly than in post-combustion systems, the high concentrations of CO_2 produced by the shift reactor (15 to 60% by volume on a dry basis), and the high pressures often encountered in these applications are more favourable for CO_2 separation. Pre-combustion would be used at power plants that employ integrated gasification combined cycle (IGCC) technology.

Oxyfuel combustion systems use oxygen instead of air for combustion of the primary fuel to produce a flue gas that is mainly water vapour and CO_2. This results in a flue gas with high CO_2 concentrations (greater than 80% by volume). The water vapour is then removed by cooling and compressing the gas stream. Oxyfuel combustion requires the upstream separation of oxygen from air, with a purity of 95 – 99% oxygen assumed in most current designs. Further treatment of the flue gas may be needed to remove air pollutants and non-condensed gases (such as nitrogen) from the flue gas before the CO_2 is sent to storage. As a method of CO_2 capture in boilers, oxyfuel combustion systems are in the demonstration phase (see Table TS.1). Oxyfuel systems also are being studied in gas turbine systems, but these applications are currently still in the research phase, in the stage of conceptual design.

Figure TS.3 shows a schematic diagram of the main capture processes and systems. All require a step involving the separation of CO_2, H_2 or O_2 from a bulk gas stream (such as flue gas, synthesis gas, air or raw natural gas). These separation steps can be accomplished by means of physical or chemical solvents, membranes, solid sorbents, or by cryogenic separation. The choice of a specific capture technology is determined largely by the process conditions under which it must operate. Current post-combustion and pre-combustion systems for power plants could capture 85%-95% of the CO_2 that is produced. Higher capture efficiencies are possible, although separation devices become considerably larger, more energy intensive and more costly. Capture and compression need roughly 10 - 40% more energy than the equivalent plant without capture. Due to the associated CO_2 emissions, the net amount of CO_2 captured is approximately 80-90%. Oxyfuel combustion systems, in principle, are able to capture nearly all of the CO_2 produced; however, the need for additional gas treatment systems to remove pollutants such as sulphur and nitrogen oxides lowers the CO_2 captured to slightly more than 90%.

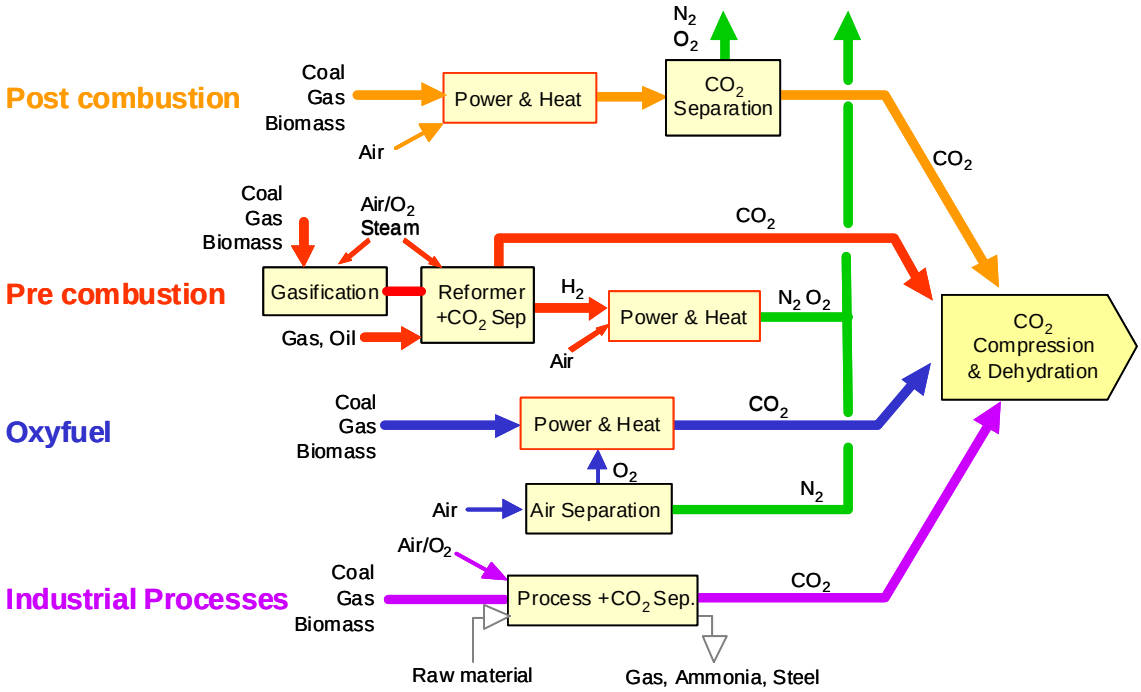
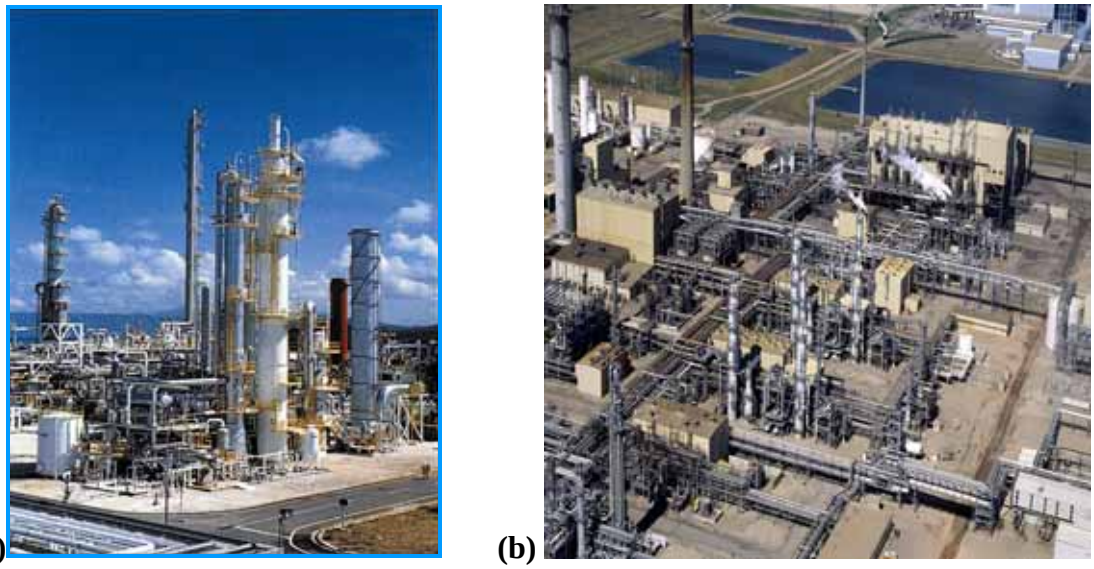


Figure TS.3. Overview of CO_2 capture processes and systems.

As noted in Section 1, CO_2 capture already is used in several industrial applications. The same technologies as would be used for pre-combustion capture are employed for the large-scale production of hydrogen (used mainly for ammonia and fertilizer manufacture, and petroleum refinery operations). The separation of CO_2 from raw natural gas (which typically contains significant amounts of CO_2) also is practiced at large scale using technologies similar to thos used for post-combustion capture. Although commercial systems also are available for large scale oxygen separation, oxyfuel combustion for CO_2 capture is currently in the demonstration phase. In addition, research is being conducted to achieve higher levels of system integration, increased efficiency and reduced cost for all types of capture systems.



(a) **(b)**

Figure TS.4. (a) CO_2 post-combustion capture at a plant in Malaysia. This plant employs a chemical absorption process to separate 0.2 $MtCO_2$ per year from the flue gas stream of a gas-fired power plant for urea production. (Courtesy of Mitsubishi Heavy Industries). (b) CO_2 pre-combustion capture at a coal gasification plant in North Dakota, USA. This plant employs a physical solvent process to separate 3.3 $MtCO_2$ per year from a gas stream to produce synthetic natural gas. Part of the captured CO_2 is used for an EOR project in Canada.

Energy, environment and risk aspects of CO_2 capture

The monitoring, risk and legal aspects associated with CO_2 capture systems appear to present no fundamentally new challenges, as they are all elements of regular health, safety and environmental control practices in industry. However, CO_2 capture systems require significant amounts of energy for their operation. This reduces net plant efficiency, so power plants require more fuel to generate each kilowatt-hour of electricity product. Based on a review of the literature, the increase in fuel consumption per kWh for plants capturing 90% CO_2 using best current technology ranges from 24-40% for new supercritical PC plants, 11-22% for NGCC plants, and 14-25% for coal-based IGCC systems relative to similar plants without CCS. The increased fuel requirement results in an increase in most other environmental emissions per kWh generated relative to new state-of-the-art plants without CO_2 capture, and, in the case of coal, in proportionally greater amounts of solid wastes. In addition, there is greater consumption of chemicals such as ammonia and limestone used by PC plants for nitrogen oxide and sulphur dioxide emissions control. Advanced plant designs that further reduce CCS energy requirements will also reduce overall environmental impacts as well as cost. Relative to many older existing plants, more efficient new or rebuilt plants with CCS may actually yield net reductions in plant-level environmental emissions.

Costs of CO_2 capture

The estimated costs of CO_2 capture at large electric power plants are based on engineering design studies of technologies in commercial use today (though often in different applications and/or at smaller scales than those assumed in the literature), as well as on design studies for concepts currently in the research and development (R&D) stage. Table TS.3a summarizes the results for new supercritical PC, NGCC and IGCC plants based on current technology with and without CO_2 capture. Capture systems for all three designs reduce CO_2 emissions per kWh by approximately 80 - 90%, taking into account the energy requirements for capture. All data for PC and IGCC plants in Table TS.3 are for bituminous coals only. The capture costs include the cost of compressing CO_2 (typically to about 11-14 MPa) but do not include the additional costs of CO_2 transport and storage (see Sections 4-7).

The cost ranges for each of the three systems reflect differences in the technical, economic and operating assumptions employed in different studies. While some differences in reported costs can be attributed to differences in the CO_2 capture system design, the major sources of variability are differences in the assumed design, operation and financing of the reference plant to which the capture technology is applied (i.e., factors such as plant size, location, efficiency, fuel type, fuel cost, capacity factor and cost of capital). Because no single set of assumptions applies to all situations or all parts of the world, a range of costs is represented.

For the studies reflected in Table TS.3a, CO_2 capture increases the cost of electricity production by 35-70% (0.01 to 0.02 US$/kWh) for an NGCC plant, 40-85% (0.02 to 0.03 US$/kWh) for a supercritical PC plant, and 20-55% (0.01 to 0.02 US$/kWh) for an IGCC plant. Overall, the electricity production costs for fossil fuel plants with capture (excluding CO_2 transport and storage costs) ranges from 0.04 - 0.09 US$/kWh, as compared to 0.03 - 0.06 US$/kWh for similar plants without capture. In most studies to date, NGCC systems typically have a lower electricity production costs than new PC and IGCC plants (with or without capture) for large base load plants with high capacity factors (75% or more) and natural gas prices between 2.6 and 4.4 US$/GJ over the life of the plant. However, for higher gas prices and/or lower capacity factors, NGCC plants often have higher electricity production costs than coal-based plants, with or without capture. Recent studies also found that IGCC plants were on average slightly more costly without capture and slightly less costly with capture than similarly sized PC plants. However, the difference in cost between PC and IGCC plants with or without CO_2 capture can vary significantly with coal type and

other local factors, such as the cost of capital for each plant type. Since neither NGCC, PC nor IGCC systems have yet been built at a full scale with CCS, the absolute or relative costs of these systems cannot be stated with a high degree of confidence at this time.

The cost of retrofitting existing power plants with CO_2 capture have not been extensively studied. A limited number of reports indicate that retrofitting an amine scrubber to an existing plant results in greater efficiency loss and higher costs than those shown in Table TS.3. A more cost-effective option was found to combine a capture system retrofit with rebuilding the boiler and turbine to increase plant efficiency and output. For some existing plants, studies indicated that similar benefits could be achieved by repowering with an IGCC system that includes CO_2 capture technology. The feasibility and cost of any of these options is highly dependent on site-specific factors, including the plant size, age, efficiency and the availability of additional space.

Table TS.3. Summary of CO_2 capture costs for new power plants based on current technology*

Performance and Cost Measures	**New NGCC Plant**				**New PC Plant**				**New IGCC Plant**			
	Range			*Rep.*	**Range**			*Rep.*	**Range**			*Rep.*
	low		**high**	*Value*	**low**		**high**	*Value*	**low**		**high**	*Value*
Emission rate w/o capture (kg CO_2/kWh)	0.344	-	0.379	*0.367*	0.736	-	0.811	*0.762*	0.682	-	0.846	*0.773*
Emission rate with capture (kg CO_2/kWh)	0.040	-	0.066	*0.052*	0.092	-	0.145	*0.112*	0.065	-	0.152	*0.108*
Percent CO_2 reduction per kWh (%)	83	-	88	*86*	81	-	88	*85*	81	-	91	*86*
Plant efficiency w/ capture, LHV basis (%)	47	-	50	*48*	30	-	35	*33*	31	-	40	*35*
Capture energy reqm't. (% more input/MWh)	11	-	22	*16*	24	-	40	*31*	14	-	25	*19*
Total capital reqm't. w/o capture (US$/kW)	515	-	724	*568*	1161	-	1486	*1286*	1169	-	1565	*1326*
Total capital reqm't. with capture (US$/kW)	909	-	1261	*998*	1894	-	2578	*2096*	1414	-	2270	*1825*
Percent increase in capital cost w/ capture (%)	64	-	100	*76*	44	-	74	*63*	19	-	66	*37*
COE w/o capture (US$/kWh)	0.031	-	0.050	*0.037*	0.043	-	0.052	*0.046*	0.041	-	0.061	*0.047*
COE with capture only (US$/kWh)	0.043	-	0.072	*0.054*	0.062	-	0.086	*0.073*	0.054	-	0.079	*0.062*
Increase in COE w/ capture (US$/kWh)	0.012	-	0.024	*0.017*	0.018	-	0.034	*0.027*	0.009	-	0.022	*0.016*
Percent increase in COE w/ capture (%)	37	-	69	*46*	42	-	66	*57*	20	-	55	*33*
Cost of net CO_2 captured (US$/t$CO_2$)	37	-	74	*53*	29	-	51	*41*	13	-	37	*23*
Capture Cost Confidence Level (see Table 3.6)	moderate				moderate				moderate			

* Because these costs do not include the costs (or credits) for CO_2 transport and storage, this table should not be used to assess or compare total plant costs for different systems with capture. The full costs of CCS plants are reported in Section 8. Abbreviations: Rep.Value=Representative value, based on the average of the values in the different studies.; COE=cost of electricity production; MWh=megawatt-hours; LHV=lower heating value; See Section 3.6.1 for calculation of energy requirement for capture plants. Notes: [a] Ranges and representative values are based on data from Special Report Tables 3.7, 3.9 and 3.10. All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. [b] All PC and IGCC data are for bituminous coals only at costs of 1.0-1.5US$/GJ (LHV); all PC plants are supercritical units. [c] NGCC data based on natural gas prices of 2.8-4.4US$/GJ (LHV basis). [d] Cost are in constant US$2002. [e] Power plant sizes range from approximately 400-800 MW without capture and 300-700 MW with capture. [f] Capacity factors vary from 65-85% for coal plants and 50-95% for gas plants (average for each=80%). [g] Fixed charge factors vary from 11-16%. [h] All costs include CO_2 compression but not additional CO_2 transport and storage costs.

Table TS.4 illustrates the cost of CO_2 capture in the production of hydrogen. Here, the cost of CO_2 capture is mainly due to the cost of CO_2 drying and compression, since separation of CO_2 is already carried out as part of the hydrogen production process. The cost of CO_2 capture adds approximately 5% to 30% to the cost of the hydrogen product.

CCS also can be applied to systems that use biomass fuels or feedstock, either alone or in combination with fossil fuels. The costs of such systems combining capture, transport and storage have been studied in a limited number of studies. The capturing of 0.19 $MtCO_2$/yr of in a 24 MW_e biomass IGCC plant is estimated to be about 80 US$/$tCO_2$ net captured (300 US$/tC), corresponding to an increase in electricity production costs of about 0.08 US$/kWh.. For other industrial processes using fossil fuels, studies of CO_2 capture are relatively few and typically limited to capture costs reported only as a cost per tonne of CO_2 captured or avoided. In general, the CO_2 produced in different processes is highly diverse in pressure and concentration (see Section 2). As a result, the cost of capture in different processes (cement and steel plants, refineries), shows a very broad range of 25 - 115 US$/$tCO_2$ net captured. In processes where a relatively pure CO_2 stream is produced (e.g., natural gas processing and ammonia production), the unit cost of capture is relatively low, similar to the hydrogen plants in Table TS.4 but can vary from 5 - 25 US$/$tCO_2$ net captured.

Table TS.4. Summary of CO_2 capture costs for new hydrogen plants based on current technology

Performance and Cost Measures	**New Hydrogen Plant**		
	Range		*Rep. Value*
	low	**high**	
Emission rate w/o capture ($kgCO_2$/GJ)	78 - 174		*137*
Emission rate with capture ($kgCO_2$/GJ)	7 - 28		*17*
Percent CO_2 reduction per GJ (%)	72 - 96		*86*
Plant efficiency w/ capture, LHV basis (%)	52 - 68		*60*
Capture energy reqm't. (% more input/GJ)	4 - 22		*8*
Cost of hydrogen w/o capture (US$/GJ)	6.5 - 10.0		*7.8*
Cost of hydrogen with capture (US$/GJ)	7.5 - 13.3		*9.1*
Increase in H_2 cost w/ capture (US$/GJ)	0.3 - 3.3		*1.3*
Percent increase in H_2 cost w/capture (%)	5 - 33		*15*
Cost of net CO_2 captured (US$/$tCO_2$)	2 - 56		*15*
Capture Cost Confidence Level	moderate to high		

Abbreviations: See footnotes to Table TS.3. Notes: [a] Ranges and representative values are based on data from Special Report Table 3.11. All costs in this table are for capture only and do not include the costs of CO_2 transport and storage. Costs are in constant US$2002 [b] Hydrogen plant feedstocks are natural gas (US$4.7-5.3/GJ) or coal (US$0.9-1.3/GJ); some plants in dataset produce electricity in addition to hydrogen. [c] Fixed charge factors vary from 13-20%. [d] All costs include CO_2 compression but not additional CO_2 transport and storage costs (see Section 8 for full CCS costs).

New or improved methods of CO_2 capture, combined with advanced power systems and industrial process designs, could reduce CO_2 capture costs and energy requirements. While costs for first-of-a-kind commercial plants often exceed initial cost estimates, the cost of subsequent plants typically declines as a result of learning-by-doing and other factors. Although there is considerable uncertainty about the magnitude and timing of future cost reductions, this literature suggests that, provided R&D efforts are sustained, improvements to commercial technologies can reduce current CO_2 capture costs by at least 20-30% over approximately the next decade, while new technologies under development could achieve more substantial cost reductions. Future cost reductions will depend on deployment and adoption of commercial technologies in the marketplace as well as sustained R&D.

4. Transport of CO_2

Except for plants located directly above a geological storage site, captured CO_2 must be transported from the point of capture to a storage site. This section reviews the principal methods of CO_2 transport and assesses their health, safety and environment aspects, and costs.

Methods of CO_2 transport

Pipelines today operate as a mature market technology and are the most prevalent method used to transport CO_2. Gaseous CO_2 is typically compressed to a pressure above 8 MPa in order to avoid two-phase flow regimes and increase the density of the CO_2. thereby making it easier and less costly to transport. CO_2 also can be transported as a liquid in ships, road tankers or rail tank cars that carry CO_2 in insulated tanks at a temperature well below ambient, and at much lower pressures.

The first long-distance CO_2 pipeline came into operation in the early 1970s. In the United States, over 2,500 km of pipeline transports more than 40 $MtCO_2$ per year from natural and anthropogenic sources to sites in primarily in Texas, where the CO_2 is used for EOR.These pipelines operate in the "dense phase" mode (in which there is a continuous progression from gas to liquid, without a distinct phase change), and at ambient temperature and high pressure. In most of these pipelines, the flow is driven by compressors at the upstream end, although some pipelines have intermediate (booster) compressor stations.

In some situations or locations, particularly for large distances or overseas, transport of CO_2 via ship may be economically more attractive. Transport of liquefied petroleum gases (LPG, principally propane and butane) by marine tankers is carried out on a large commercial scale. CO_2 can be transported by ship in much the same way (typically at 0.7 MPa pressure), but this is currently done only at a small scale because of limited demand. The properties of liquefied CO_2 are similar to those of LPG, and the technology can be scaled up to large CO_2 carriers if a demand for such systems were to materialize.

Road and rail tankers also are technically feasible options. These systems transport CO_2 at a low temperature of -20ºC and at 2 MPa pressure. However, they are uneconomical in comparison with pipelines and ships, except on a very small scale, and are unlikely to be relevant to large-scale CCS.

Environment, safety and risk aspects

Just as there are standards for natural gas admitted to pipelines, so minimum standards for "pipeline quality" CO_2 should emerge as the CO_2 pipeline infrastructure develops further. Current standards, developed largely in the context of EOR applications, are not necessarily identical to what would be required for CCS. A low-nitrogen content is important for EOR, but would not be so significant for CCS. However, a CO_2 pipeline through populated areas might need a lower specified maximum H_2S content. Pipeline transport of CO_2 through populated areas also requires attention to detailed route selection, over-pressure protection, leak detection and other design factors. No major obstacles to pipeline design for CCS are foreseen, however.

CO_2 could leak to the atmosphere during transport, although leakage losses from pipelines are very small. Dry (moisture-free) CO_2 is not corrosive to the carbon-manganese steels customarily used for pipelines, even if the CO_2 contains contaminants such as oxygen, hydrogen sulphide, and sulphur or nitrogen oxides. Moisture-laden CO_2, on the other hand, is highly corrosive, so a CO_2 pipeline in this case would have to be made from a corrosion-resistant alloy, or internally clad with an alloy or a continuous polymer coating. Some pipelines are made from corrosion-resistant alloys, although the cost of materials is several times larger than carbon-manganese steels. For ships, the total loss to the atmosphere is between 3 and 4% per 1000 km, counting both boil-off and the exhaust from ship

engines. The boil-off could be reduced by capture and liquefaction, and recapture would reduce the loss to 1 to 2% per 1000 km.

Accidents can also occur. For existing CO_2 pipelines, which are mostly in areas of low population density, there have been fewer than one reported incidents per year (0.0003 per km-year) and no injuries or fatalities. This is consistent with experience with hydrocarbon pipelines, and the impacts would probably not be more severe than those with natural gas accidents. In the UK, natural gas pipeline systems have not caused any fatalities, in the US one (in 2003). In marine transportation, hydrocarbon gas tankers are potentially dangerous, but the recognized hazard has led to standards of design, construction and operation, and serious incidents are rare.

Cost of CO_2 transport

Costs have been estimated for both pipeline and marine transportation of CO_2. In every case the costs depend strongly on the distance and the quantity transported. In the case of pipelines, the costs depend on whether the pipeline is onshore or offshore, whether the area is heavily congested, and whether there are mountains, large rivers, or frozen ground present. All these factors could double the cost per unit length, with even larger increases for pipelines in populated areas. Any additional costs for recompression (booster pump stations) that may be needed for longer pipelines would be counted as part of transport costs. Such costs are relatively small and not included in the estimates presented here.

Figure TS.5 shows the cost of pipeline transport for a nominal distance of 250 km. This typically amounts to 1-8 US$/tCO$_2$ (4-30 US$/tC). The figure also shows how pipeline cost depends on the CO_2 mass flow rate. Steel cost accounts for a significant fraction of the cost of a pipeline, so fluctuations in such cost (such as the doubling in the years from 2003 to 2005) could affect overall pipeline economics.

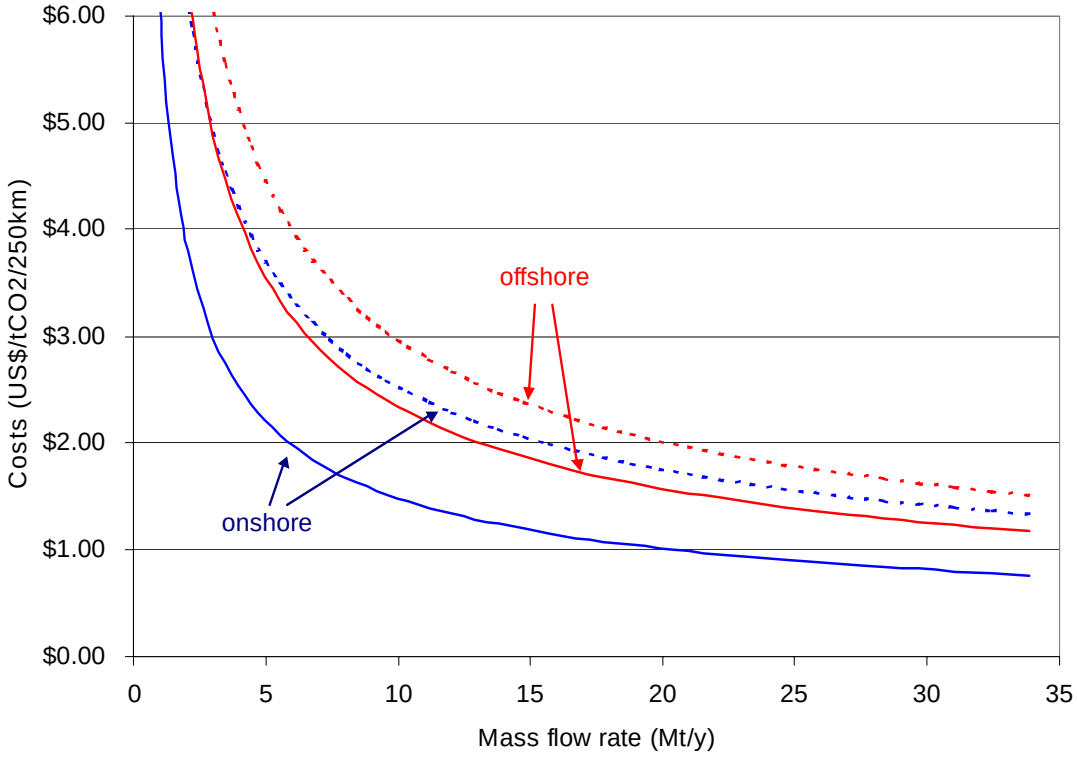


Figure TS.5. Transport costs for onshore pipelines and offshore pipelines, in US$ per tCO$_2$ per 250 km. Indicated are high estimates (dotted lines) and low estimates (solid lines).

For ship transport, the tanker volume and the characteristics of the loading and unloading systems are among the key factors that determine the overall transport cost. The costs associated with CO_2 compression and liquefaction are accounted for in the capture costs presented earlier. Figure TS.6 compares pipeline and marine transportation costs, and shows the break-even distance. If the marine option is available, it is typically cheaper than pipelines for distances greater than approximately 1000 km. For ocean storage the most suitable transport system depends on the injection method: from a stationary floating vessel, a moving ship, or a pipeline from shore.

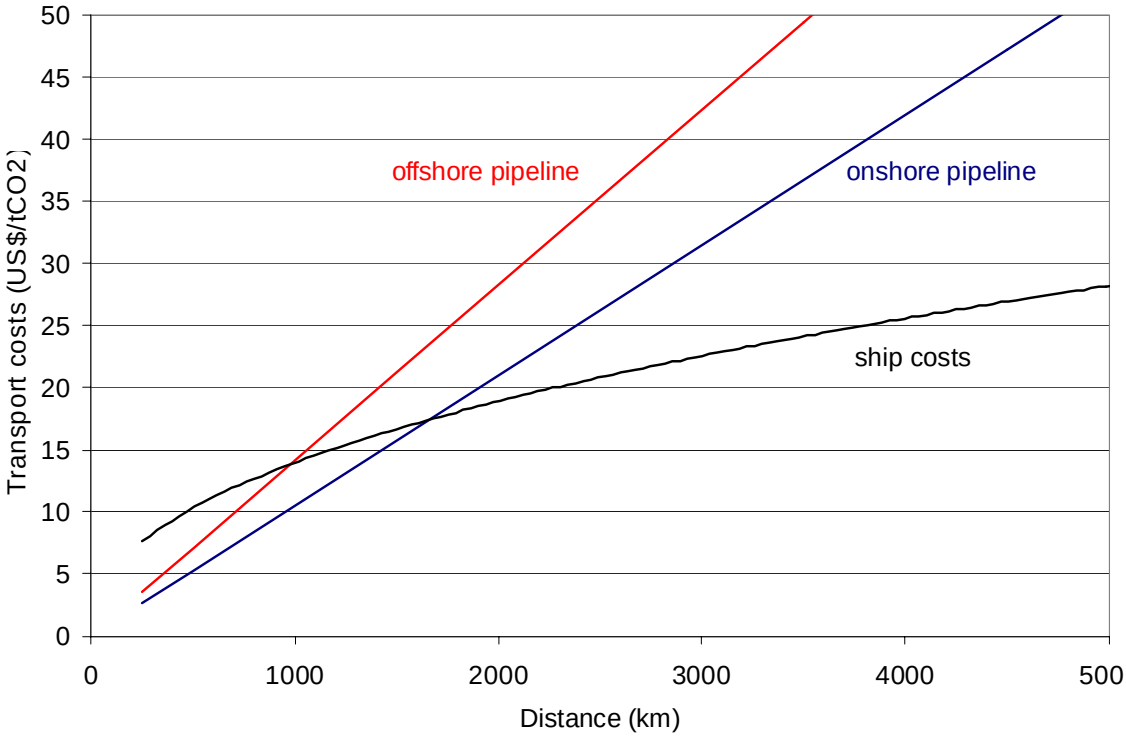


Figure TS.6. Costs, plotted as transportation cost in US$/t$CO_2$ transported against distance, for onshore pipelines, offshore pipelines and ship transport. Pipeline costs are given for a mass flow of 6 MtCO_2/yr. Ship costs include intermediate storage facilities, harbour fees, fuel costs, and loading and unloading activities. Costs include also additional costs for liquefaction compared to compression.

5. Geological storage

This section examines three types of geological formations that have received extensive consideration for geological storage of CO_2: oil and gas reservoirs, deep saline formations and unminable coal beds (Figure TS.7). In each case, geological storage of CO_2 is accomplished by injecting it in dense form into a rock formation below the earth's surface. Porous rock formations that hold or (as in the case of depleted oil and gas reservoirs) have previously held fluids, such as natural gas, oil or brines, could potentially be candidates for CO_2 storage. Suitable storage formations can occur in both onshore and offshore sedimentary basins (i.e., natural large-scale depressions in the earth's crust that are filled with sediments). Coal beds also may be used for storage of CO_2 (see Figure TS.7) where it is unlikely that the coal will later be mined and provided that the permeability is sufficient. The option of storing CO_2 in coal beds, and enhancing methane production is still in the demonstration phase (see Table TS.1).

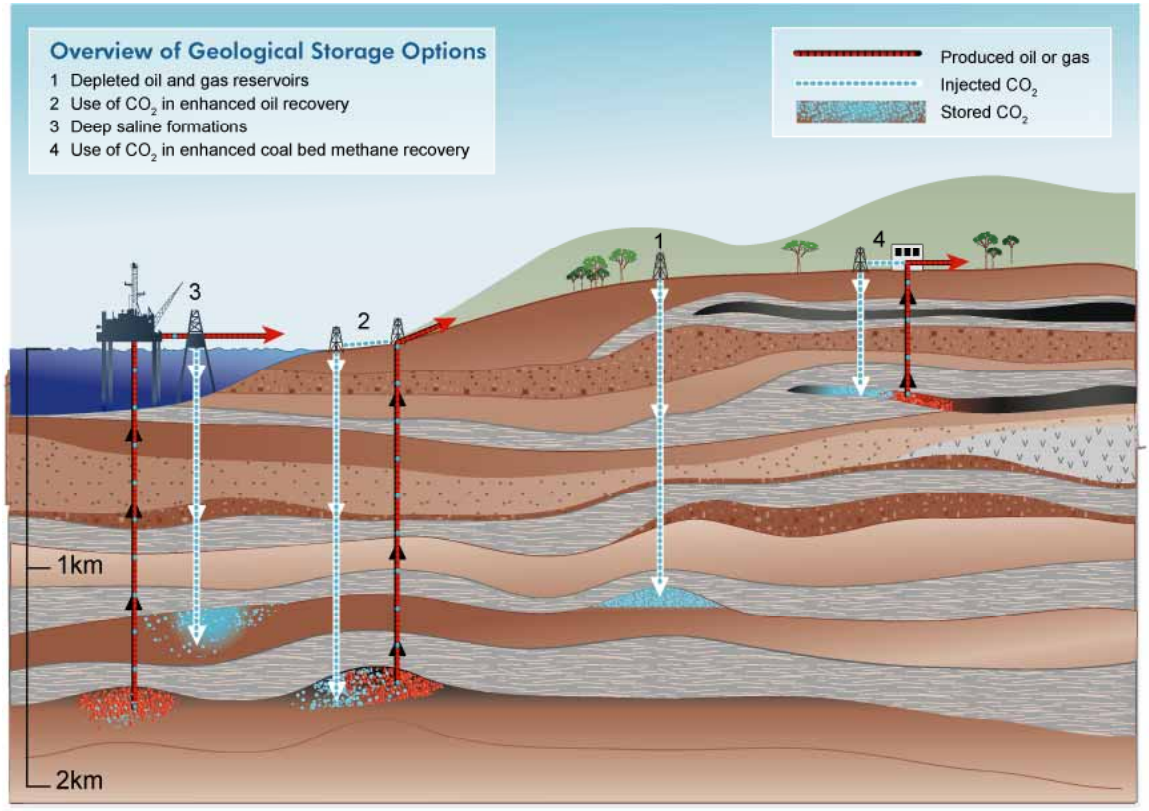


Figure TS.7. Methods for storing CO_2 in deep underground geological formations. Two methods may be combined with the recovery of hydrocarbons: EOR (2) and ECBM (4). See text for explanation of these methods (Courtesy CO2CRC).

Existing CO_2 storage projects

Geological storage of CO_2 is ongoing in three industrial-scale projects (i.e., on the order of 1 $MtCO_2$/yr or more): the Sleipner project in the North Sea, the Weyburn project in Canada and the In Salah project in Algeria. Yearly, about 3 - 4 $MtCO_2$ that would otherwise be released to the atmosphere is captured and stored annually in geological formations. These and other projects are listed in Table TS.5.

In addition to the CCS projects currently in place, 30 $MtCO_2$ is injected annually for EOR, mostly in Texas, USA, where EOR commenced in the early 1970s. Most of this CO_2 is obtained from natural CO_2 reservoirs found in western regions of the US, with some coming from anthropogenic sources such as natural gas processing. Much of the CO injected for EOR is produced with the oil, from which it is separated and then reinjected. At the end of the oil recovery, the CO_2 can be retained for the purpose of climate change mitigation, rather than vented to the atmosphere. This is planned for the Weyburn project.

Table TS.5. Sites where CO_2 storage is currently in progress or planned, varying from small pilots to large-scale commercial applications.

Project name	Country	Injection Start (year)	Approximate average daily injection rate (tCO_2/day)	Total (planned) storage (tCO_2)	Storage reservoir type
Weyburn	Canada	2000	3,000 - 5,000	20,000,000	EOR
In Salah	Algeria	2004	3,000 - 4,000	17,000,000	Gas field
Sleipner	Norway	1996	3,000	20,000,000	Saline formationn
K12B	Netherlands	2004	100 (1,000 planned for 2006+)	8,000,000	Enhanced Gas Recovery
Frio	U.S.A	2004	177	1600	Saline formation
Fenn Big Valley	Canada	1998	50	200	ECBM
Qinshui Basin	China	2003	30	150	ECBM
Yubari	Japan	2004	10	200	ECBM
Recopol	Poland	2003	1	10	ECBM
Gorgon (Planned)	Australia	ca. 2009	10,000	unknown	Saline formation
Snohvit (Planned)	Norway	2006	2,000	unknown	Saline formation

Technology and mechanisms of storage

Injection of CO_2 in deep geological formations uses many of the same technologies that have been developed by the oil and gas exploration and production industry. Well-drilling technology, injection technology, computer simulation of storage reservoir dynamics and monitoring methods can potentially be adapted from existing applications to meet the requirements for geological storage of CO_2. Other underground injection practices also provide relevant operational experience, notably natural gas storage, and deep injection of liquid wastes, Acid gas disposal (mixtures of CO_2 and H_2S) has been conducted in Canada and the U.S. since 1990, also at the megatonne scale.

CO_2 storage in hydrocarbon reservoirs or deep saline formations is expected to take place at depths generally below 800 m, where the ambient pressures and temperatures will usually result in CO_2 being in a liquid or supercritical state. Under these conditions, the density of CO_2 will range from 60 to 80% of the density of water, close to the density of some crude oils, which results in buoyant forces that tend to drive CO_2 upwards. Consequently, having a well-sealed caprock over the selected storage reservoir rock is important to ensure that CO_2 remains trapped underground. When injected underground, the CO_2 compresses and fills the pore space by partially displacing the fluids that are already present (called *in situ* fluids). For oil and gas reservoirs, the displacement of *in situ* fluids by injected CO_2 can, result in most of the pore volume being available for CO_2 storage. For saline formations, estimates of potential storage volume are lower, ranging from as low as several percent to over 30% of the total rock volume.

Once injected into the storage formation, the fraction retained depends on a combination of physical and geochemical trapping mechanisms. Physical trapping to block upward migration of CO_2 is provided by a layer of shale and clay rock above the storage formation. This impermeable layer is known as “caprock”. Additional physical trapping can be provided by capillary forces that retain CO_2 in the pore spaces of the formation. In many cases, however, one or more sides of the

formation remain open, allowing for lateral migration of CO_2 beneath the caprock. In these cases, additional mechanisms are important for long-term entrapment of the injected CO_2.

The mechanism known as geochemical trapping occurs as the CO_2 reacts with the *in situ* fluids and host rock. First, CO_2 dissolves in the *in situ* water. Once this occurs (over time scales of tens of thousands of years), the CO_2-laden water becomes more dense and therefore sinks down into the formation (rather than rising toward the surface). Next, chemical reactions between the dissolved CO_2 and rock minerals form ionic species, so that over millions of years, a fraction of the injected CO_2 would be converted to solid carbonate minerals.

Yet another type of trapping occurs when CO_2 is preferentially adsorbed onto coal or organic-rich shales replacing gases such as methane. In these cases, CO_2 will remain trapped as long as there are stable pressures and temperatures. These processes normally would take place at shallower depths than CO_2 storage in hydrocarbon reservoirs and saline formations.

Geographic distribution and capacity of storage sites

As shown earlier in Section 2 (Figure TS.3), regions with sedimentary rocks that are potentially suitable for CO_2 storage exist around the globe, both onshore and offshore. This report focuses on oil and gas reservoirs, deep saline formations and unminable coal beds. Other possible geological formations or structures (such as basalts, oil or gas shales, salt caverns and abandoned mines) represent niche opportunities, or are insufficiently studied at this time to assess their potential.

The estimates of the technical potential[6] for different geological storage options are summarized in Table TS.6. The estimates and levels of confidence are based on an assessment of the literature, both of regional bottom-up, and global top-down estimates. No probabilistic approach to estimating capacity estimates exists in the literature, which would be required to reliably quantify levels of uncertainty. Overall estimates for especially the upper limit to the potential vary widely and have a high degree of uncertainty, reflecting conflicting methodologies in the literature and the fact that our knowledge of saline formations is quite limited in most parts of the world. For oil and gas reservoirs, better quality estimates are available based on replacement of hydrocarbon volumes with CO_2 volumes. It should be noted, that with the exception of CO_2-EOR, that these reservoirs will not be available for CO_2 storage until the hydrocarbons are depleted, and that pressure changes and geomechanical effects due to hydrocarbon production in the reservoir may reduce the actual capacity.

Another way of looking at storage potential, however, is to ask whether it is likely to be adequate for the amounts of CO_2 that would need to be avoided using CCS under different greenhouse gas stabilization scenarios and assumptions about deployment of other mitigation options. As discussed later in Section 8, the estimated range of economic potential[7] for CCS over the next century is roughly 200 to 2,000 $GtCO_2$. The lower limits in Table TS.6 suggest that worldwide it is virtually certain that there is 200 $GtCO_2$ and likely that there is 2,000 $GtCO_2$ of geological storage capacity**.**

[6] Technical potential is the amount by which it is possible to reduce greenhouse gas emissions by implementing a technology or practice that already has been demonstrated.

[7] Economic potential is the amount of greenhouse gas emissions reductions from a specific option that would make sense economically, given prevailing circumstances (i.e. a price of CO_2 reductions and costs of other options).

Table TS.6. Storage capacity for several geological storage options. The storage capacity includes storage options that are not economical.

Reservoir type	Lower estimate of storage capacity ($GtCO_2$)	Upper estimate of storage capacity ($GtCO_2$)
Oil and gas fields	675[a]	900[a]
Unminable coal seams (ECBM)	3 - 15	200
Deep saline formations	1,000	Uncertain, but possibly 10^4

[a] These numbers would increase by 25% if "undiscovered" oil and gas fields were included in this assessment.

Site selection criteria and methods

Site characterization, selection and performance prediction are crucial for successful geological storage. Before selecting a site, the geological setting must be characterized to determine if the overlying caprock will provide an effective seal, if there is a sufficiently voluminous and permeable storage formation, and whether any abandoned or active wells will compromise the integrity of the seal.

Techniques developed for exploration of oil and gas reservoirs, natural gas storage sites and liquid waste disposal sites are well suited for characterizing geological storage sites for CO_2. Examples include seismic imaging, pumping tests for evaluating storage formations and seals, and cement integrity logs. To support site characterization and selection activities, computer programmes that model underground CO_2 movement are used. These programmes were initially developed for applications such as oil and gas reservoir engineering and groundwater resources investigations. Although they include many of the physical, chemical and geomechanical processes needed to predict both short-term and long-term performance of CO_2 storage, more experience is needed to gain confidence in their ability to predict long-term performance when adapted for CO_2 storage. Moreover, the reliability of models depends critically on good site characterization data.

Risk assessment and environmental impacts

The risks due to leakage from storage of CO_2 in geological reservoirs fall in two broad categories: global risks and local risks. Global risks involve the release of CO_2 that may contribute significantly to climate change if some fraction leaks from the storage formation to the atmosphere. In addition, if CO_2 leaks out of a storage formation, local hazards may exist for humans, ecosystems and groundwater. These are the local risks.

With regard to global risks, based on observations and analysis of current CO_2 storage sites, natural systems, engineering systems and models, it is suggested that the fraction retained in appropriately selected and managed reservoirs is very likely[8] to exceed 99% over 100 years, and is likely[9] to exceed 99% over 1000 years. Similar fractions retained are likely for even longer periods of time, as the risk of leakage is expected to decrease over time as other mechanisms provide additional trapping. Whether these fractions retained would be sufficient to make impermanent storage valuable for climate change mitigation is discussed in Section 8.

With regard to local risks, there are two types of scenarios in which leakage may occur. In the first case, injection well failures or leakage up abandoned wells could create a sudden and rapid release of CO_2. This type of release is likely to be detected quickly and stopped using techniques that are available today for containing well blowouts (uncontrolled flow up a well). Hazards associated with this type of release are primarily to workers in the vicinity of the release at the time it occurs, or to those called in to control the blow-out. A concentration of CO_2 greater than 7 - 10% in air would

[8] "Very likely" is a probability of 90 to 99%
[9] "Likely" is a probability of 66 to 90 %

cause immediate dangers to human life and health. Containing these kinds of releases may take hours to days and the overall amount of CO_2 released is like to be very small compared to the total amount injected. These types of hazards are managed effectively on a regular basis in the oil and gas industry using engineering and administrative controls.

In the second scenario, leakage could occur through undetected faults, fractures or even through leaking wells where the release to the surface is more gradual and diffuse. In this case, hazards are primarily to drinking water aquifers and ecosystems where CO_2 accumulates in the zone between the surface and the top of the water table. Groundwater impacts can result both from CO_2 leaking directly into an aquifer, as well as from brines that enter the aquifer as a result of being displaced by CO_2 during the injection process. Acidification of soils and displacement of oxygen in soils also may occur in this scenario. Additionally, if leakage to the atmosphere were to occur in low-lying areas with little wind, or in sumps and basements overlying these diffuse leaks, harm would be caused to humans and animals if a leak goes undetected. Human impacts of leakage from offshore storage locations would be less severe than from onshore storage locations. Leakage routes can be identified by several techniques and by characterization of the reservoir. Figure TS.8 shows some of the potential leakage paths for a saline formation. When the potential leakage routes are known, the monitoring and remediation strategy can be adapted to address the potential leakage.

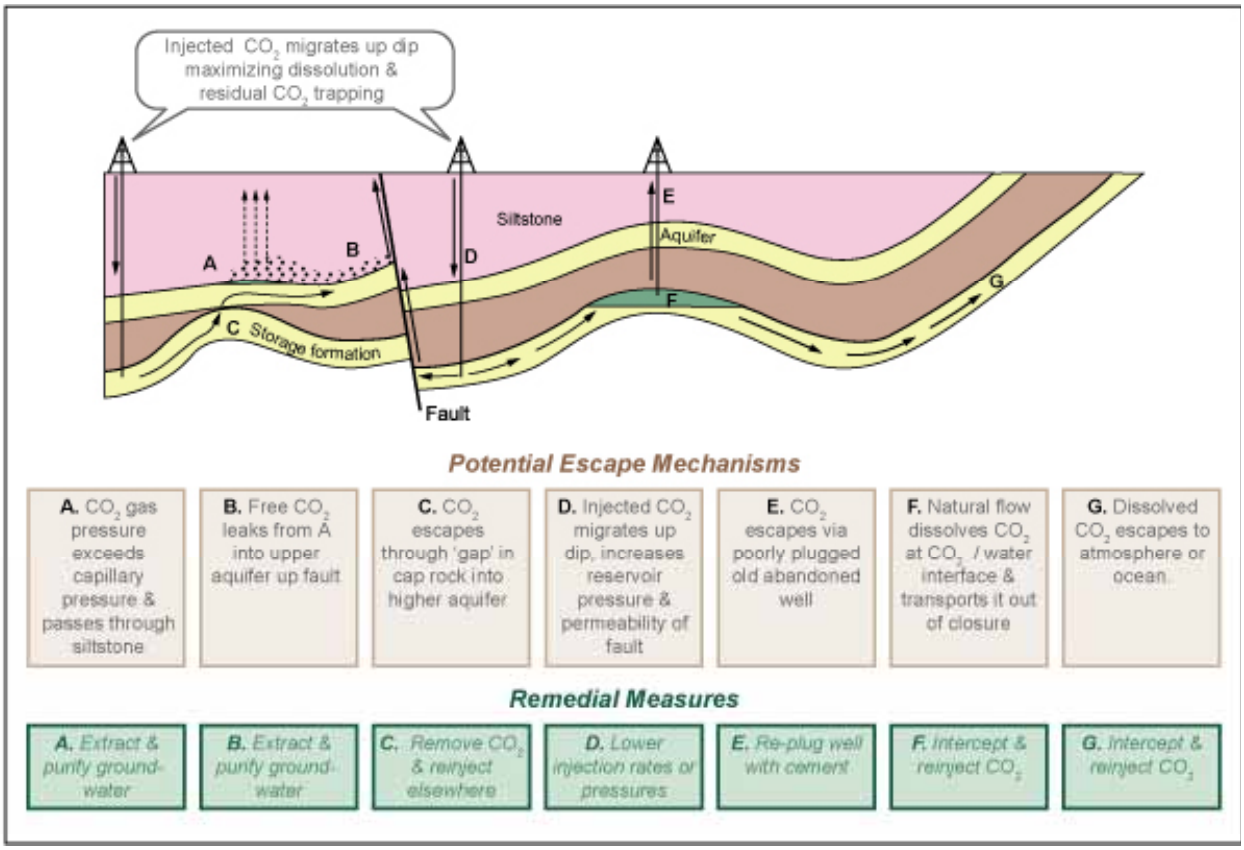


Figure TS.8. Potential leakage routes and remediation techniques for CO_2 injected into saline formations. The remediation technique would depend on the potential leakage routes identified in a reservoir (Courtesy CO2CRC).

Careful storage system design and siting, together with methods for early detection of leakage (preferably long before CO_2 reaches the land surface), are effective ways to reduce hazards associated with diffuse leakage. The available monitoring methods are promising, but more experience is needed to establish detection levels and resolution. Once detected, some remediation

techniques are available to stop or control leakage. Depending on the type of leakage, these could involve standard well repair techniques, or extraction of CO_2 by intercepting its leak into a shallow groundwater aquifer (see Figure TS.8). Techniques to remove CO_2 from soils and groundwater also are available, but likely to be costly. Experience will be needed to demonstrate the effectiveness and ascertain the costs of these techniques for use in CO_2 storage.

Monitoring and verification

Monitoring is a very important part of the overall risk management strategy for geological storage projects. Standard procedures or protocols have not been developed yet, but are expected to evolve as technology improves, depending on local risks and regulations. However, it is expected that some parameters such as injection rate and injection well pressure will be measured routinely. Repeated seismic surveys have been shown to be useful for tracking the underground migration of CO_2. Newer techniques such as gravity and electrical measurements also may be useful. Sampling of groundwater and the soil between the surface and water table may be useful for directly detecting CO_2 leakage. CO_2 sensors with alarms can be located at the injection wells for ensuring worker safety and to detect leakage. Surface-based techniques may also be used for detecting and quantifying surface releases. High-quality baseline data improve the reliability and resolution of all measurements and will be essential for detecting small rates of leakage.

Since all of these monitoring techniques have been adapted from other applications, they need to be tested and assessed with regard to reliability, resolution and sensitivity in the context of geological storage. All of the existing industrial-scale projects and pilot projects have programmes designed to develop and test these and other monitoring techniques. Methods also may be needed or desireable to monitor the amount of CO_2 stored underground in the context of the emission reporting and monitoring requirements in the UNFCCC (see Section 9). Given the long-term nature of CO_2 storage, site monitoring may be required for very long periods.

Legal issues

At present few countries have specifically developed legal and regulatory frameworks for onshore CO_2 storage. Relevant laws include petroleum-related laws, drinking water laws and mining regulations. In many cases, there are laws that apply to some, if not most, of the issues related to CO_2 storage. Specifically, long-term liability issues, such as global issues associated with the leakage of CO_2 to the atmosphere, as well as local concerns about environmental impacts, have not yet been addressed. Monitoring and verification regimes and risks of leakage may play an important role in determining liability, and vice versa. There are also considerations about the longevity of institutions, on-going monitoring and transferability of institutional knowledge. The long-term perspective is essential to a legal framework for CCS as storage times extend over many generations and so does the climate change problem. In some countries, notably the US, the property rights of all those affected must be considered legally as the pore space is owned by the surface property owner.

According to general principles of customary international law, States can exercise their sovereignty in their territories and therefore could engage in activities such as the storage of CO_2 (both geological and ocean) in those areas under their jurisdiction However, if such storage causes transboundary impacts, States have the responsibility to ensure that activities within their jurisdiction or control do not cause damage to the environment of other States or of areas beyond the limits of national jurisdiction.

Currently, there are several treaties (notably the UN Convention on the Law of the Sea, and the

London[10] and OSPAR[11] Conventions) that potentially apply to the offshore injection of CO_2 into marine environments (i.e. both into the sea and the sub-seabed). All these treaties have been drafted without specific consideration of CO_2 storage. An assessment undertaken by the Jurists and Linguists Group to the OSPAR Convention (relating to the North East Atlantic region), for example, found that depending on the method and purpose of injection, CO_2 injection into the geological sub-seabed and the ocean could be compatible with the treaty in some cases, such as when the CO_2 is transported via a pipeline from land. A similar assessment is now underway by Parties to the London Convention. Furthermore, papers by legal commentators have concluded that CO_2 captured from an oil or natural gas extraction operation and stored offshore in a geological formation (like the Sleipner operation) would not be considered "dumping" under, and thus prohibited by, the London Convention.

Public perception

Assessing public perception of CCS is challenging because of the relatively technical and “remote” nature of this issue at the present time. Results of the very few studies that have been done to date on public perception of CCS indicate that the public is generally not well informed about CCS. If information is given alongside information on other climate change mitigation options, the handful of studies carried out so far indicate that CCS is generally regarded less favourable than other options, such as energy efficiency improvements and use of non-fossil energy sources. Acceptance of CCS, where it occurs, is characterized as “reluctant” rather than “enthousiastic”, although public perception is likely to change in the future. In some cases this reflects the perception that CCS might be required because of failure to reduce CO_2 emissions in other ways. There are indications that geological storage could be viewed favourably if it is adopted in conjunction with more desirable measures. Further, from the limited research, it also appears that at least two conditions may have to be met before CO_2 capture and storage is considered by the public as a credible technology, alongside other better known options: (1) anthropogenic global climate change has to be regarded as a relatively serious problem; (2) there must be acceptance of the need for large reductions in CO_2 emissions to reduce the threat of global climate change.

Cost of geological storage

Because the technologies and equipment used for geological storage are widely used in the oil and gas industries, cost estimates for this option have a relatively high degree of confidence for the storage capacity in the lower range of technical potential. However, there is a significant range and variability of costs due to site-specific factors such as onshore versus offshore, reservoir depth and geological characteristics of the storage formation (e.g., permeability and formation thickness).

Representative estimates of the cost for storage in saline formations and depleted oil and gas fields are typically between 0.5 - 8 US$/$tCO_2$ injected. Monitoring costs of 0.1 - 0.3 US$/$tCO_2$ are additional. The lowest storage costs are for onshore, shallow, high permeability reservoirs, and/or storage sites where wells and infrastructure from existing oil and gas fields may be re-used.

When storage is combined with EOR, ECBM or (potentially) Enhanced Gas Recovery (EGR), the revenue from additional oil or gas can reduce the total cost of CCS. Based on data and oil prices prior to 2003, enhanced oil production for onshore EOR could yield net benefits of 10 - 16 US$/$tCO_2$ (37 - 59 US$/tC) (including the costs of geological storage). For EGR and ECBM, which are still under development, there is no reliable cost information based on actual experience. In all cases, however, the economic benefit of enhanced production is strongly dependent on oil and gas

[10] Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter.
[11] Convention for the Protection of the Marine Environment of the North-East Atlantic, which was adopted in Paris. OSPAR is an abbreviation of Oslo-Paris.

prices. In this regard, the literature basis for this report does not take into account the rise in world oil and gas prices since 2003 and assumes oil prices of 15 - 20 US$ per barrel. Should higher prices be sustained over the life of a project, revenues for enhanced hydrocarbon recovery could be higher than those reported here.

6. Ocean storage

A potential CO_2 storage option is to directly inject captured CO_2 into the deep ocean, (e.g., depths greater than 1,000 m) where most of it would be isolated from the atmosphere for centuries. This can be achieved by transporting CO_2 via pipeline or ship to an ocean storage site, where it is injected into the water column of the ocean or at the sea floor. The dissolved and dispersed CO_2 would subsequently become part of the global carbon cycle. Figure TS.9 shows some of the main methods that could be employed. Ocean storage has not yet been deployed or demonstrated at a pilot scale, and is still in the research phase. However, there have been small-scale field experiments and 25 years of theoretical, laboratory and modelling studies of intentional ocean storage of CO_2.

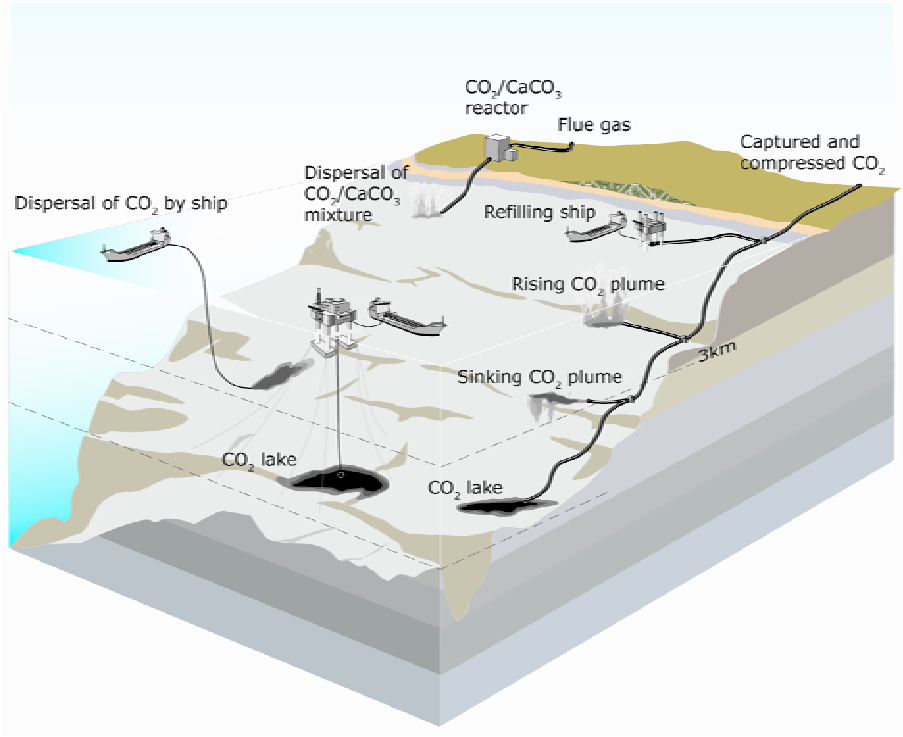


Figure TS.9. Methods of ocean storage.

Storage mechanisms and technology

Oceans cover over 70% of the earth's surface with an average depth of 3,800 m. Because carbon dioxide is soluble in water, there are natural exchanges of CO_2 between the atmosphere and waters at the ocean surface that occur until equilibrium is reached. If the atmospheric concentration of CO_2 is increased, the ocean gradually takes up additional CO_2. In this way, the oceans have taken up about 500 $GtCO_2$ (140 GtC) of the total 1,300 $GtCO_2$ (350 GtC) of anthropogenic emissions released to the atmosphere over the past 200 years. As a result of the increased atmospheric CO_2 concentrations from human activities relative to pre-industrial levels, the oceans are currently taking up CO_2 at a rate of about 7 $GtCO_2$/yr (2 GtC/yr).

Most of this carbon dioxide now resides in the upper ocean and thus far has resulted in a decrease in

pH of about 0.1 at the ocean surface because of the acidic nature of CO_2. To date, however, there has been virtually no change in pH deep in the oceans. Models predict that over the next several centuries the oceans will eventually take up most of the CO_2 released to the atmosphere as CO_2 is dissolved at the ocean surface and subsequently mixed with deep ocean waters.

There is no practical physical limit on the amount of anthropogenic CO_2 that could be stored in the ocean. However, on a millennial time scale the amount stored will depend on oceanic equilibration with the atmosphere. Stabilizing atmospheric CO_2 concentrations between 350 ppmv and 1000 ppmv would imply that between 2,000 and 12,000 $GtCO_2$ would eventually reside in the ocean - in the absence of intentional CO_2 injection. This range thus represents the upper limit of technical storage potential of ocean storage of CO_2 through active injection. Estimates of the technical potential could also take into account environmental factors, such as a maximum allowable pH change, which would lower the technical potential, depending on the methods of injection.

Analysis of ocean observations and models agree that injected CO_2 will be isolated from the atmosphere for at least several hundreds of years, and that the fraction retained tends to be higher with deeper injection (see Table TS.7). Concepts to increase fractions retained include forming solid CO_2 hydrates and/or liquid CO_2 lakes on the sea floor, and dissolving alkaline minerals such as limestone to neutralize the acidic CO_2. Dissolving mineral carbonates, if found practical, could extend the storage timescale to roughly 10,000 years, while minimizing changes in ocean pH and CO_2 partial pressure. However, large amounts of limestone and energy for materials handling would be required for this approach (roughly the same order of magnitude as the amounts per tonne of CO_2 injected as needed for mineral carbonation; see Section 7).

Table TS.7. Fraction of CO_2 retained for ocean storage as simulated by seven ocean models for 100 years of continuous injection at three different depths starting in the year 2000.

	Injection Depth		
Year	**800 m**	**1500 m**	**3000 m**
2100	0.78 ± 0.06	0.91 ± 0.05	0.99 ± 0.01
2200	0.50 ± 0.06	0.74 ± 0.07	0.94 ± 0.06
2300	0.36 ± 0.06	0.60 ± 0.08	0.87 ± 0.10
2400	0.28 ± 0.07	0.49 ± 0.09	0.79 ± 0.12
2500	0.23 ± 0.07	0.42 ± 0.09	0.71 ± 0.14

Ecological and environmental impacts and risks

Injection of a few $GtCO_2$ would produce a measurable change in ocean chemistry in the region of injection, whereas injection of hundreds of $GtCO_2$ would produce larger changes in the region of injection and eventually produce measurable changes over the entire ocean volume. Model simulations that assume a release from seven locations at 3,000 m depth and ocean storage providing 10% of the mitigation effort for stabilization at 550 ppmv CO_2, projected acidity changes (pH changes) of more than 0.4 over approximately 1% of the ocean. For comparison, in a 550 ppmv stabilization case without ocean storage a pH change of more than 0.25 at the ocean surface was estimated, due to equilibration with the elevated CO_2 concentrations in the atmosphere. In either case, a pH change of 0.2 to 0.4 is significantly greater than pre-industrial variations in ocean acidity. Over centuries, ocean mixing will result in the loss of isolation of injected CO_2. As more CO_2 reaches the ocean surface waters, releases into the atmosphere would occur gradually from large regions of the ocean. There are no known mechanisms for sudden or catastrophic release of injected CO_2 into the atmosphere.

Experiments show that adding CO_2 can harm marine organisms. Effects of elevated CO_2 levels have

mostly been studied on time scales up to several months in individual organisms that live near the ocean surface. Observed phenomena include reduced rates of calcification, reproduction, growth, circulatory oxygen supply and mobility, as well as increased mortality over time. In some organisms these effects are seen in response to small additions of CO_2. Immediate mortality is expected close to injection points or CO_2 lakes. The chronic effects of direct CO_2 injection into the ocean on ocean organisms or ecosystems over large ocean areas and long time scales have not yet been studied.

No controlled ecosystem experiments have been performed in the deep ocean, so only a preliminary assessment of potential ecosystem effects can be given. It is expected that ecosystem consequences will increase with increasing CO_2 concentrations and decreasing pH, but the nature of such consequences is currently not understood, and no environmental criteria have as yet been identified to avoid adverse effects. At present, it is also unclear how or whether species and ecosystems would adapt to the sustained chemical changes.

Costs of ocean storage

Although no experience is existent with ocean storage, some attempts have been made to estimate the costs of CO_2 storage projects that release CO_2 at the seafloor or deep ocean. The costs of CO_2 capture and transport to the shoreline (e.g., via pipeline) are not included in the cost of ocean storage. However, the costs of offshore pipelines or ships, plus any additional energy costs, are included in the ocean storage cost. The costs of ocean storage are summarized in Table TS.8. These numbers indicate that for short distances, the fixed pipeline option would be cheaper. For larger distances, either the moving ship or the transport by ship to a platform with subsequent injection would be more attactive.

Table TS.8. Costs for ocean storage at depths deeper than 3,000 m.

	Costs (US$/tCO$_2$ net injected)	
	100 km	**500 km**
Fixed pipeline	6	31
Moving ship/platform[a]	12 - 14	13 - 16

[a]The costs for the moving ship option are for injection depths of 2,000 - 2,500 m.

Legal aspects and public perception

The global and regional treaties on the law of the sea and marine environment, such as the OSPAR and the London Convention discussed earlier in Section 5 for geological storage sites, also affect ocean storage, as they concern the “maritime area”. Both Conventions distinguish between the storage method employed and the purpose of storage to determine the legal status of ocean storage of CO_2. As yet, however, the legal status of intentional ocean storage has not been decided.

The very small number of public perception studies that have looked at ocean storage of CO_2 indicate that there is very little public awareness or knowledge of this subject. In the few studies conducted thus far, however, the public has expressed greater reservations regarding ocean storage than geological storage. These studies also indicate that the perception of ocean storage changed when more information was provided; in one study this led to increased acceptance of ocean storage, while in another study it led to less acceptance. The literature also notes that “significant opposition” developed around a proposed ocean CO_2 release experiment in the Pacific Ocean.

7. Mineral carbonation and industrial uses

This section deals with two rather different options for CO_2 storage. The first is mineral carbonation, which involves converting CO_2 to solid inorganic carbonates using chemical reactions.

The second option is the industrial use of CO_2, either directly, or as feedstock for production of various carbon-containing chemicals.

Mineral carbonation: technology, impacts and costs

Mineral carbonation refers to the fixation of CO_2 using alkaline and alkaline-earth oxides, such as magnesium oxide (MgO) and calcium oxide (CaO), which are present in naturally occurring silicate rocks such as serpentine and olivine. Chemical reations between these materials and CO_2 produces compounds such as magnesium carbonate ($MgCO_3$) and calcium carbonate ($CaCO_3$, commonly known as limestone). The quantity of the silicate rocks that can be found in the earth's crust exceeds the amounts needed to fix all the CO_2 that would be produced by the combustion of all available fossil fuel reserves. These oxides are also present in small quantities in some industrial wastes, such as stainless steel slags and ashes. Mineral carbonation produces silica and carbonates that are stable on long timescales, and thus may be disposed of in areas such as silicate mines, or re-used for construction purposes (see Figure TS.10), though likely in small quantities relative to the amounts produced. After the carbonation of CO_2, it would not be released to the atmosphere. As a consequence, the needs for monitoring of the disposal site are likely to be limited and the associated risks are very low. The technical potential is difficult to estimate at this early phase of development, but mineral carbonation could have a technical potential of thousands of gigatonnes of CO_2. The potential would be limited by the fraction of silicate reserves that can be technically exploited, by environmental issues such as the volume of product disposal, and by legal and societal constraints at the storage location.

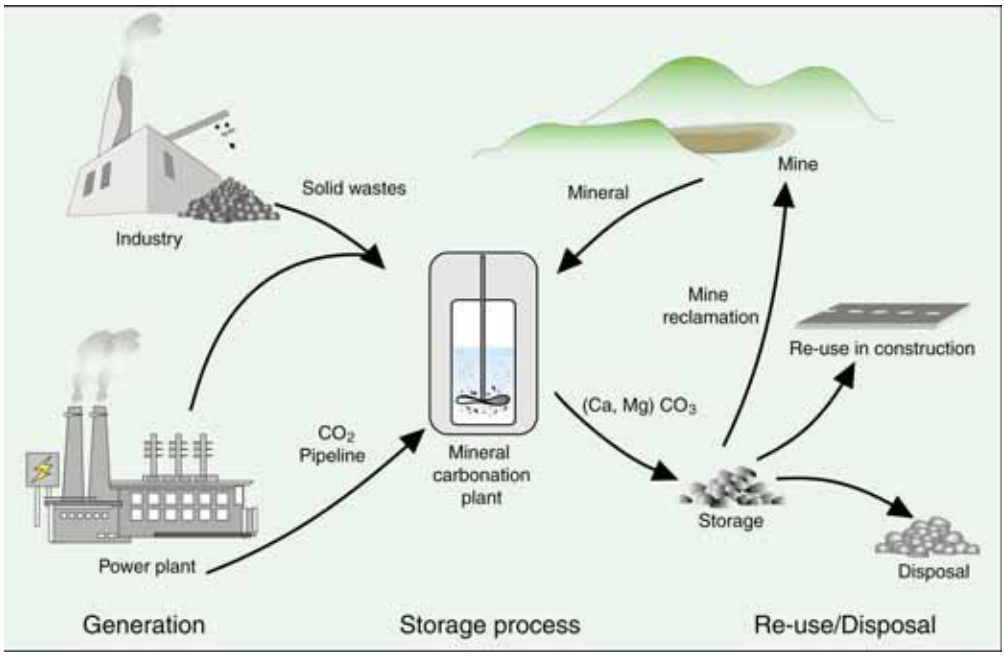


Figure TS.10. Material fluxes and process steps associated with the mineral carbonation of silicate rocks or industrial residues (Courtesy ECN).

The process of mineral carbonation occurs naturally, where it is known as "weathering" . In nature, the process occurs very slowly; therefore, it must be accelerated considerably to be a viable storage method for CO_2 captured from anthropogenic sources. Research in the field of mineral carbonation thus focuses on finding process routes that can achieve reaction rates of industrial interest, and make the reaction more energy-efficient. Mineral carbonation technology using natural silicates is in the research phase, but some processes using industrial wastes are in the demonstration phase.

A commercial process would require mining, crushing and milling of the mineral-bearing ores and their transport to a processing plant receiving a concentrated CO_2 stream from a capture plant (see Figure TS.10). The resulting extra energy requirements are 30 to 50% more than the reference electricity plant without capture or mineral carbonation. This is additional to the energy requirements for capture of CO_2. The energy requirements significantly increase the cost per tonne of CO_2 avoided for the overall system (see Section 8). The best case studied so far is the wet carbonation of natural silicate olivine. This process is estimated to cost approximately 50-100 US$/t$CO_2$ net mineralized (in addition to CO_2 capture and transport costs, but taking into account the additional energy requirements). The mineral carbonation process would require 1.6 to 3.7 tonnes of silicates per tonne of CO_2 to be mined, and produce 2.6 to 4.7 tonnes of materials to be disposed per tonne of CO_2 stored as carbonates. This would therefore be a large operation, whose environmental impacts would be similar to that of current large-scale surface mining operations. Serpentine also often contains chrysotile, a natural form of asbestos. Its presence therefore demands monitoring and mitigation measures, such as those available in the mining industry. On the other hand, the products of mineral carbonation are chrysotile-free, since this is the most reactive component of the rock and is thus the first substance converted to carbonates.

A number of issues still need to be clarified before any estimates of the technical storage potential of mineral carbonation can be given. The issues include assessments of the technical feasibility and corresponding energy requirements at large scales, but also the fraction of silicate reserves that can be technically and economically exploited for CO_2 storage. The environmental impacts of mining and product disposal could also restrain the potential. Mineral carbonation could have a technical potential on the order of thousands of gigatonnes of CO_2.

Industrial uses

Industrial uses of CO_2 cover chemical and biological processes where CO_2 is a reactant, such as in urea and methanol production, as well as various technological applications that use CO_2 directly, such as in the horticulture industry, for refrigeration, food packaging, welding, beverages and fire extinguishers. Currently, CO_2 is used at a rate of approximately 120 MtCO_2 per year (30 MtC/yr) worldwide, excluding use for EOR (discussed in Section 5). The dominant use (two thirds of the total) is for urea production (used in the manufacture of fertilizers and other products). Part of the CO_2 is extracted from natural wells, and part originates from industrial sources, mainly high-concentration sources such as from ammonia and hydrogen production plants, that capture CO_2 as part of the production process.

Industrial uses of CO_2 can, in principle, contribute to keeping CO_2 out of the atmosphere by storing it in the so-called carbon chemical pool (i.e., the stock of carbon-bearing manufactured products). However, as a climate change mitigation measure, this option is meaningful only if the quantity and duration of CO_2 stored are significant, and if there is a real net reduction of CO_2 emissions. The typical lifetime of most of the CO_2 currently used by industrial processes has storage times of only days to months, before the stored carbon is degraded to CO_2 and again emitted to the atmosphere. Such short time scales do not contribute meaningfully to climate change mitigation. In addition, the total industrial use figure of 120 MtCO_2/yr is small compared to emissions from major anthropogenic sources (see Table TS.2). While some industrial processes store a small proportion of CO_2 (totalling roughly 20 MtCO_2/yr) for up to several decades, the total amount of long-term (century-scale) storage is presently on the order of 1 MtCO_2/yr or less, with no prospects for major increases.

Another important question is whether industrial uses of CO_2 can result in an overall net reduction of CO_2 emissions via the substitution for other industrial processes or products. This can be evaluated correctly only by considering proper system boundaries for the energy and material

balances of the CO_2 utilization processes, and by carrying out a detailed life cycle analysis of the proposed use of CO_2. Literature on this is limited, but shows that precise figures are difficult to estimate and that even the sign can be uncertain, i.e. industrial uses, could also lead to an increase of overall emissions. In view of the low fraction retained, the small volumes, and the possibility that substitution may lead to increases in CO_2 emissions, it can be concluded that the contribution of industrial uses of captured CO_2 to climate change mitigation is expected to be small.

8. Costs and economic potential

The stringency of future greenhouse gas emissions control requirements and the expected costs of CCS systems will determine, to a large extent, the future deployment of CCS technologies relative to other greenhouse gas mitigation options. This section first summarizes the overall cost of CCS for the major options and process applications considered in previous sections. Then CCS is examined in the context of alternative options for global greenhouse gas reductions.

Cost of CCS systems

As noted earlier, there is still relatively little experience in combining CO_2 capture, transport and storage into a fully integrated CCS system. And while some CCS components are already deployed in mature markets for certain industrial applications, the use of CCS for large-scale power plants (the application of major potential interest) still remains to be implemented.

The literature reports a fairly wide range of costs for CCS components (see Sections 3-7). The range is due primarily to the variability in site-specific factors, especially the design, operating and financing characteristics of the power plant or industrial facility to which CCS is applied; the type and costs of fuel used; the required distance, terrain and quantity of CO_2 transported; and the type and characteristics of the CO_2 storage. In addition, there is uncertainty in the estimates of current and (especially) future performance and cost of all CCS technology components. The literature reflects a widely-held belief, however, that the cost of building and operating CO_2 capture systems will decline over time as a result of learning-by-doing (from technology deployment) and sustained R&D. Historical evidence also suggests that costs for first-of-a-kind capture plants could exceed current estimates before costs subsequently decline. In most CCS systems, the cost of capture (including compression) is the largest cost component. Costs of electricity and fuel cost vary considerably from country to country, which also influences the economic viability of CCS options.

Table TS.9 summarizes the costs of CO_2 the components capture, transport and storage reported in Sections 3 to 7. Monitoring costs are also reflected. In Table TS.10, the component costs are combined to show the total costs of CCS and electricity generation for three power systems with pipeline transport and two geological storage options.

Table TS.9. Current cost ranges for the components of a CCS system, applied to a given type of power plant or industrial source. The costs of the separate components cannot simply be summed to calculate the costs of the whole CCS system in US$/$CO_2$ avoided. All numbers are representative of costs for full-scale, new power plants with natural gas prices assumed to be 2.8 - 4.4 US$/GJ and coal prices 1 - 1.5 US$/GJ.

Costs component	Cost range	Remarks
Capture from a coal- or gas-fired power plant	15 - 75 US$/$tCO_2$ net captured	Includes net costs of captured CO_2 for plants with capture, compared to the same plant without capture.
Capture from ammonia production or gas processing	5 - 25 US$/$tCO_2$ net captured	
Capture from other industrial sources	25 - 115 US$/$tCO_2$ net captured	
Transportation	1 - 8 US$/$tCO_2$ transported	Per 250 km pipeline or shipping for mass flow rates of 5 (high end) to 40 (low end) $MtCO_2$/yr.
Geological storage	0.5 - 8 US$/$tCO_2$ injected	Excluding potential revenues from EOR or ECBM.
Ocean storage	5 - 30 US$/$tCO_2$ injected	Including offshore transportation of 100 - 500 km
Geological storage: monitoring and verification	0.1 - 0.3 US$/$tCO_2$ injected	Depend on the regulatory requirements
Mineral carbonation	50 - 100 US$/$tCO_2$ net mineralized	Range for the best case studied. Includes additional energy use for carbonation

Table TS.10. Range of total costs for CO_2 capture, transport and geological storage based on current technology for new power plants using bituminous coal or natural gas

Power Plant Performance and Cost Parameters[a]	Pulverized Coal Power Plant	Natural Gas Combined Cycle Power Plant
Reference Plant without CCS		
Cost of Electricity (US$/kWh)	0.043 - 0.052	0.031 - 0.050
Power Plant with Capture		
Increased Fuel Requirement (%)	24 - 40	11 - 22
CO_2 Captured (kg/kWh)	0.82 - 0.97	0.36 - 0.41
CO_2 Avoided (kg/kWh)	0.62 - 0.70	0.30 - 0.32
% CO_2 Avoided	81 - 88	83 - 88
Power Plant with Capture and Geological Storage[b]		
Cost of Electricity (US$/kWh)	0.063 - 0.099	0.043 - 0.077
Cost of CCS (US$/kWh)	0.019 - 0.047	0.012 - 0.029
% increase in COE	43 - 91	37 - 85
Mitigation Cost (US$/$tCO_2$ avoided)	30 - 71	38 - 91
(US$/tC avoided)	110 - 260	140 - 330
Power Plant with Capture and Enhanced Oil Recovery[c]		
Cost of Electricity (US$/kWh)	0.049 - 0.081	0.037 - 0.070
Cost of CCS (US$/kWh)	0.005 - 0.029	0.006 - 0.022
% increase in COE	12 - 57	19 - 63
Mitigation Cost (US$/$tCO_2$ avoided)	9 - 44	19 - 68
(US$/tC avoided)	31 - 160	71 - 250

[a] All changes are relative to a similar (reference) plant without CCS. See Table TS.3 for details of assumptions underlying reported cost ranges.

[b] Capture costs based on ranges from Table TS.3; transport costs range from US$0-5/$tCO_2$; geological storage cost ranges from US$0.6-8.3/$tCO_2$.

[c] Same capture and transport costs as above; Net storage costs for EOR range from -10 to -16 US$/$tCO_2$, (based on pre-2003 oil prices of 15-20 US$/barrel).

For the plants with geological storage and no EOR credit, the total cost of CCS ranges from 0.02-0.05 US$/kWh for PC plants and 0.01-0.03 US$/kWh for NGCC plants (both employing post-combustion capture). For IGCC plants (using pre-combustion capture), the total CCS cost ranges from 0.01-0.03 US$/kWh relative to a similar plant without CCS. For all electricity systems, the cost of CCS can be reduced by about 0.01 - 0.02 US$/kWh because the EOR revenues partly compensate for the CCS costs. The largest cost reductions are seen for coal-based plants, which capture the largest amounts of CO_2. In a few cases, the low end of the CCS cost range can be negative, indicating that the assumed credit for EOR over the life of the plant is greater than the lowest reported cost of CO_2 capture for that system. In a few cases of industrial uses, this might also be the case.

In addition to fossil fuel-based energy conversion processes, CO_2 could also be captured in power plants fueled with biomass, or fossil fuel plants with biomass co-firing. At present, biomass plants are small in scale (less than 100 MW_e), hence, the resulting costs of production with and without CCS are relatively high compared to fossil alternatives. Full CCS costs for biomass could amount up to 110 US$/t$CO_2$ avoided. The use of biomass or the cofiring of biomass combined with CCS could lead to lower or negative CO_2 emissions, provided the biomass is grown sustainably, which partly compensates for the additional costs for this option, depending on the value of CO_2 reductions. The level of compensation depends on the value of CO_2 emission reductions. Similarly, CO_2 could be captured in biomass-fueled H_2 plants. The cost is reported to be 22-25 US$/t$CO_2$ (80-92 US$/tC) avoided in a plant producing 1 million Nm^3/day of H_2, and corresponds to an increase in the H_2 product costs of about 2.7 US$/GJ. Significantly larger biomass plants could potentially benefit from economies of scale, bringing down costs of the CCS systems to broadly similar levels as coal plants. The emissions from biomass amenable to capture are estimated to be in the range of 900 - 1,600 GtCO_2 cumulatively over the course of the century. However, to date there has been little experience with large scale biomass plants, so their feasibility has not been proven yet, and costs and potential are difficult to estimate.

For non-power applications, the cost of CCS is less well studied. Because these sources are very diverse in CO_2 concentration and partial pressure, the available cost studies show a very broad range. The lowest costs were found for processes that already separate CO_2 as part of the production process, such as hydrogen production, for which the cost of capture was reported earlier in Table TS.4. The full CCS cost, including transport and storage, increases the cost of hydrogen production by 0.4 to 4.4 US$/GJ for the case with geological storage, and by -2.0 to 2.8 US$/GJ with EOR credits, based on the same cost assumptions as for Table TS.10.

Cost of CO_2 avoided

Also shown in Table TS.10 are the ranges of costs for "CO_2 avoided". Because of CCS energy requirements, the amount of fuel input (and therefore CO_2 emissions) increases per unit of net power output. As a result, the amount of CO_2 produced per unit of product (e.g., a kWh of electricity) is greater for the power plant with CCS than the reference plant, as shown graphically in Figure TS.11. To determine the CO_2 reductions one can attribute to CCS, one needs to compare CO_2 emissions per kWh of the plant with capture to that of the reference plant without capture. The difference is termed the avoided emissions. Because the energy requirements for capture, transport and storage can never be zero, the amount of CO_2 avoided is always less than the amount of CO_2 captured.

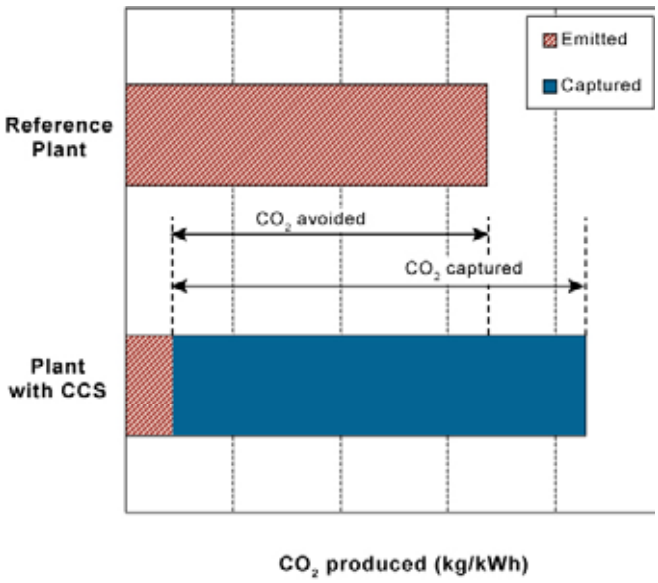


Figure TS.11. Schematic illustrating the concept of CO_2 avoided and its relationship to CO_2 captured.

Application of CCS to power plants may influence the decision on which type of plant to install in the reference case and which fuel to use. Therefore, in some situations, it can be useful to calculate a cost per tonne of CO_2 avoided based on a reference plant different from the CCS plant. Table TS.10 displays the cost and emission factors for the three reference plants and the corresponding CCS plants for the case of geological storage. Table TS.11 summarizes the range of estimated costs for different combinations of CCS plants and least cost reference plants of potential interest. It shows that, for instance, if initially a PC plant was planned, applying CCS to that plant may lead to the conclusion that the NGCC plant might be a more attractive option, provided natural gas is available. Another option would be to build an IGCC plant with capture in stead of equipping a PC plant with capture.

Table TS.11. Mitigation cost ranges for different combinations of reference and CCS plants based on current technology for new power plants. Currently, in many regions, common practice would be either a PC plant or an NGCC plant[12]. EOR benefits are based on oil prices of 15 - 20 US$ per barrel. Gas prices are assumed to be 2.8 -4.4 $/GJ, coal prices 1-1.5 $/GJ (based on Table 8.3a).

	NGCC Reference Plant	**PC Reference Plant**
	US$/tCO$_2$ avoided (US$/tC avoided)	**US$/tCO$_2$ avoided (US$/tC avoided)**
Power plant with capture and geological storage		
NGCC	40 - 90 (140 - 330)	20 - 60 (80 - 220)
PC	70 - 270 (260 - 980)	30 - 70 (110 - 260)
IGCC	40 - 220 (150 - 790)	20 - 70 (80 - 260)
Power plant with capture and EOR		
NGCC	20 - 70 (70 - 250)	0 - 30 (0 - 120)
PC	50 - 240 (180 - 890)	10 - 40 (30 - 160)
IGCC	20 - 190 (80 - 710)	0 - 40 (0- 160)

Economic potential of CCS for climate change mitigation

Assessments of economic potential of CCS are based on energy and economic models that study future CCS deployment and costs in the context of scenarios that achieve economically efficient, least-cost paths to stabilization of atmospheric CO_2 concentrations by the end of this century.

While there are significant uncertainties in the quantitative results from these models (see discussion below), all models indicate that CCS systems are unlikely to deploy on a large scale in the absence of an explicit policy that substantially limits greenhouse gas emissions to the atmosphere. With greenhouse gas emission limits imposed, many integrated assessments foresee CCS systems deploying on a large scale within a few decades from the start of any significant climate change mitigation regime. Energy and economic models indicate that CCS systems are unlikely to contribute significantly to mitigation of climate change unless deployed in the power sector. For this to happen, the price of carbon dioxide reductions would have to exceed 25 - 30 US$/tCO$_2$ over the lifetime of the CCS project, or an equivalent limit on CO_2 emissions would have to be mandated. The literature and current industrial experience indicate that in the absence of measures to limit CO_2 emissions there are only small, niche opportunities for CCS technologies to deploy. These early opportunities involve CO_2 captured from a high-purity, low cost source, transport of CO_2 over less than 50 km, coupled with CO_2 storage in a value-added application such as EOR. The potential of such niche options is about 360 MtCO$_2$ cumulatively (see Section 2).

Models also indicate that CCS systems will be competitive with other large-scale mitigation options such as nuclear power and renewable energy technologies. These studies show that including CCS in a mitigation portfolio could reduce by 30% or more the cost of stabilizing CO_2 concentrations. One aspect of the cost competitiveness of CCS technologies is that they can complement and facilitate the deployment of other potentially important long-term climate change mitigation technologies such as low carbon or carbon-free hydrogen production from carbonaceous fuels and large-scale biomass energy systems.

[12] IGCC is not included as a reference power plant that would be built today since this technology is not yet widely deployed in the electricity sector and is usually slightly more costly than a PC plant.

In most scenarios, the emissions abatement gets progressively more constraining over time. In most cases, while there is significant penetration of CCS systems in the first half of this century, the majority of CCS deployment occurs in the second half for scenarios that achieve stabilization by 2100. The earliest CCS deployments typically are seen in the industrialized nations, with deployment eventually spreading worldwide. While results for different scenarios and models differ (often significantly) in the specific mix and quantities of different measures needed to achieve a particular emissions constraint (see Figure TS.12), the consensus of the literature shows that CCS could be an important component of the broad portfolio of energy technologies and emission reduction approaches.

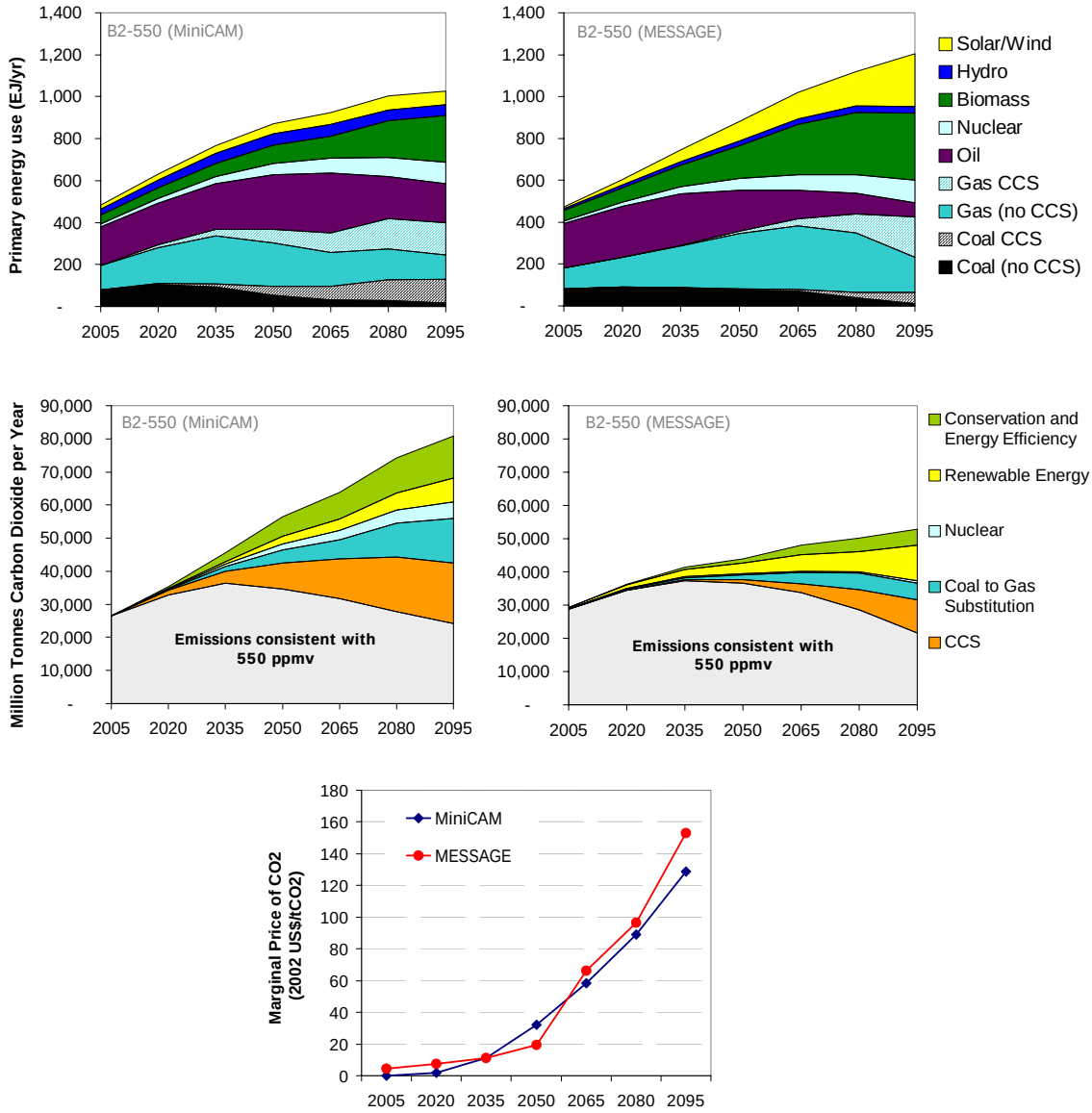


Figure TS.12. Illustration of the possible economic potential for CCS, for two scenario studies for a 550 ppmv CO_2 stabilization case. a) and b) are the possible contributions of CCS technologies and other mitigation options to the primary energy mix, highlighting that the energy use can differ with varying assumptions. c) and d) represent the contributions of CCS and other mitigation options to a portfolio for

stabilization at 550 ppmv CO_2, using an IPCC-SRES B2 baseline[13] for two model calculations; e) the marginal price of CO_2 reduction (US$/t$CO_2$ avoided) over time for the two scenario runs.

The actual use of CCS is likely to be lower than the estimates of economic potential indicated by these energy and economic models. As noted earlier, the results are typically based on an optimized least-cost analysis that does not adequately account for real-world barriers to technology development and deployment, such as environmental impacts, lack of a clear legal or regulatory framework, perceived investment risks of different technologies, and uncertainty as to how quickly the cost of CCS will be reduced through R&D and learning-by-doing. Models typically employ simplified assumptions regarding the costs of CCS for different applications and the rates at which future costs will be reduced.

For CO_2 stabilization scenarios between 450-750 ppmv, published estimates of the cumulative amount of CO_2 potentially stored globally over the course of this century (in geological formation and/or the oceans) span a wide range, from very small contributions to thousands of gigatons of CO_2. To a large extent, this wide range is due to the uncertainty of long-term socio-economic, demographic and (especially) technological changes, which are the main drivers of future CO_2 emissions. However, it is important to note that the majority of results for stabilization scenarios of 450-750 ppmv CO_2 tend to cluster in a range of 220-2,200 $GtCO_2$ (60-600 GtC) cumulative deployment of CCS. For CCS to achieve this economic potential, several hundreds to thousands of CCS systems would be required worldwide over the next century, each capturing some 1-5 $MtCO_2$ per year. As indicated in Section 5, it is very likely that the technical potential for geological storage alone is sufficient to cover the high end of the economic potential range for CCS.

Perspectives on CO_2 leakage from storage

The policy implications of slow leakage from storage depend on assumptions in the analysis. Studies conducted to address the question of how to deal with impermanent storage are based on different approaches: the value of delaying emissions, cost minimization of a specified mitigation scenario, or allowable future emissions in the context of an assumed stabilization of atmospheric greenhouse gas concentrations. Some of these studies allow future releases to be compensated by additional reductions in emissions; the results depend on assumptions regarding the future cost of reductions, discount rates, the amount of CO_2 stored, and the atmospheric concentration stabilization level assumed. In other studies, compensation is not seen as an option because of political and institutional uncertainties and the analysis focuses on limitations set by the assumed stabilization level and the amount stored. While specific results of the range of studies vary with the methods and assumptions made, the outcomes suggest that a fraction retained on the order of 90 to 99% for 100 years or 60 to 95% for 500 years could make such impermanent storage still valuable for mitigation of climate change.

9. Emission inventories and accounting

An important aspect of CO_2 capture and storage is the development and application of methods to estimate and report the quantities by which emissions of CO_2 (and associated emissions of methane or nitrous oxides) are reduced, avoided, or removed from the atmosphere. The two elements of this are, (1) the actual estimation and reporting of emissions for national greenhouse gas inventories, and (2) accounting for CCS under international agreements to limit net emissions.[14]

[13] The different baseline emissions in the two models represent the highest and lowest projections of the B2 scenario family.

[14] In this context, "estimation" is the process of calculating greenhouse gas emissions and "reporting" is the process of providing the estimates to the UNFCCC. "Accounting" refers to the rules for comparing emissions and removals as reported with commitments (IPCC 2003).

Current framework

Under the UNFCCC, national greenhouse gas emission inventories have traditionally reported emissions for a specific year, and have been prepared on an annual or other periodic basis. The IPCC Guidelines (IPCC 1996) and Good Practice Guidance Reports (IPCC 2000; 2003) describe detailed approaches for preparing national inventories that are complete, transparent, documented, assessed for uncertainties, consistent over time, and comparable across countries. The IPCC documents now in use do not specifically include CO_2 capture and storage options. However, the IPCC Guidelines are currently undergoing revisions that should provide some guidance when the revisions are published in 2006. The framework and concepts of emissions inventories that already have been accepted could be applied to CCS systems, although some issues might need revision or expansion..

Issues relevant to accounting and reporting

In the absence of current international agreements, it is not clear whether the various forms of CO_2 capture and storage will be treated as reductions in emissions or as removals from the atmosphere. In either case, CCS results in new pools of CO_2 that may be subject to physical leakage at some time in the future. Currently there are no methods available within the framework of UNFCCC to monitor, mreasure and account for physical leakage from storage sites .This leakage is likely to be small in magnitude and distant in time..

Creation of a specific category for CCS in the emissions reporting framework may be considered, but is not strictly necessary since the quantities of CO_2 captured and stored could be reflected in the sector in which the CO_2 was produced. CO_2 storage in a given location could include CO_2 from many different source categories, and even from sources in many different countries. Fugitive emissions from the capture, transport and injection of CO_2 to storage can largely be estimated within the existing reporting methods, and emissions associated with the added energy required to operate the CCS systems can be measured and reported within the existing inventory frameworks. Specific consideration may also be required for CCS applied to biomass systems as that application would result in reporting negative emissions, for which there is currently no provision in the reporting framework.

Issues relevant to international agreements

Quantified commitments to limit greenhouse gas emissions and the use of emissions trading, Joint Implementation (JI) or the Clean Development Mechanism (CDM) require clear rules and methods to account for emissions and removals. Because CCS has the potential to move CO_2 across traditional accounting boundaries (e.g., CO_2 might be captured in one country and stored in another, or captured in one year and partly released from storage in a later year), the rules and methods for accounting may be different than those used in traditional emissions inventories.

To date, most of the scientific, technical and political discussions on accounting for stored CO_2 have focused on sequestration in the terrestrial biosphere. The history of these negotiations may provide some guidance for the development of accounting methods for CCS. Recognizing the potential impermanence of CO_2 stored in the terrestrial biosphere, the UNFCCC accepted the idea that net emissions can be reduced through biological sinks, but has imposed complex rules for how such accounting is accomplished. CCS is notably different in many ways from CO_2 sequestration in the terrestrial biosphere (see Table TS.12), and the different forms of CCS are notably different from one another. However, the main goal of accounting is to ensure that CCS activities produce real and quantifiable reductions in net emissions. One tonne of CO_2 permanently stored has the same benefit in terms of atmospheric CO_2 concentrations as one tonne of CO_2 not emitted, but one ton of CO_2 temporarily stored has less benefit. It is generally accepted that this difference should be

reflected in any system of accounting for reductions in net greenhouse gas emissions.

The IPCC Guidelines (IPCC 1996) and Good Practice Guidance Reports (IPCC 2000; 2003) also contain guidelines for monitoring of greenhouse gas emissions. It is unknown whether the revised guidelines of the IPCC for CCS can be satisfied by monitoring techniques, particularly for geological and ocean storage. Several techniques are available for monitoring and verification of CO_2 emissions from geological storage, but they vary in applicability, detection limits and uncertainties. Currently, monitoring for geological storage can be done quantitatively at injection and qualitatively in the reservoir and by measuring surface fluxes of CO_2. Ocean storage monitoring can be done by detection of the CO_2 plume, but not by measuring ocean surface release to the atmosphere. Experiences from monitoring existing CCS projects are still too limited for conclusions on the physical leakage rates and associated uncertainties.

Table TS.12 Differences in the forms of CCS and biological sinks that might influence the way accounting is conducted.

Property	Terrestrial Biosphere	Deep Ocean	Geological Reservoirs
CO_2 sequestered or stored	Stock changes can be monitored over time.	Injected carbon can be measured.	Injected carbon can be measured.
Ownership	Stocks will have a discrete location and can be associated with an identifiable owner.	Stocks will be mobile and may reside in international waters.	Stocks may reside in reservoirs that cross national or property boundaries and differ from surface boundaries..
Management decisions	Storage will be subject to continuing decisions about land-use priorities.	Once injected there are no further human decisions on maintenance.	Once injected human decisions to influence continued storage involve minimal maintenance, unless storage interferes with resource recovery.
Monitoring	Changes in stocks can be monitored.	Changes in stocks will be modelled	Release of CO_2 might be detected by physical monitoring.
Expected retention time	Decades, depending on management decisions.	Centuries, depending on depth and location of injection.	Essentially permanent, barring physical disruption of the reservoir.
Physical leakage	Losses might occur due to disturbance, climate change, or land-use decisions.	Losses will assuredly occur as an eventual consequence of marine circulation and equilibration with the atmosphere.	Losses are unlikely except in the case of disruption of the reservoir or the existence of initially undetected leakage pathways.
Liability	A discrete land-owner can be identified with the stock of sequestered carbon.	Multiple parties may contribute to the same stock of sequestered CO_2 and the CO_2 may reside in international waters.	Multiple parties may contribute to the same stock of sequestered CO_2 that may lie under multiple countries.

The Kyoto Protocol creates different units of accounting for greenhouse gas emissions, emissions reductions, and emissions sequestered under different compliance mechanisms. “Assigned amount units” (AAUs) describe emissions commitments and apply to emissions trading, “certified emission reductions” (CERs) are used under the CDM, and “emission reduction units” (ERUs) are employed under JI. To date, little guidance has been provided by international negotiations regarding methods to calculate and account for project-related CO_2 reductions from CCS systems (i.e. only CERs or ERUs), and it is therefore uncertain how such reductions will be accommodated under the Kyoto Protocol. Some guidance may be given by the methodologies for biological sinks rules. Moreover,

current agreements do not deal with cross-border CCS projects. This is particularly important when dealing with cross-border projects involving CO_2 capture in an "Annex B" country that is party to the Kyoto Protocol but stored in a country that is not in Annex B or is not bound by the Protocol.

Although currently available methods for national emissions inventories can either accommodate CCS systems or be revised to do so, accounting for stored CO_2 raises questions about the acceptance and transfer of responsibility for stored emissions. Such issues may be addressed through national and international political processes.

10. Gaps in knowledge

This summary of the gaps in knowledge covers aspects of CCS where increasing knowledge, experience and reducing uncertainty would be important to facilitate decision making on large-scale deployment of CCS.

Technologies for capture and storage

Technologies for the capture of CO_2 are relatively well understood today based on industrial experience in a variety of applications. Similarly, there are no major technical or knowledge barriers to the adoption of pipeline transport, or to the adoption of geological storage of captured CO_2. However, integration of capture, transport and storage in full-scale projects is needed to gain the knowledge and experience required for more widespread deployment of CCS technologies. R&D efforts also are needed to improve knowledge of emerging concepts and enabling technologies for CO_2 capture that hold promise of significantly reducing the costs of capture for new and existing facilities. More specifically, knowledge gaps concern large coal-based and natural gas-based power plants with CO_2 capture at a scale of several hundred megawatts (or several $MtCO_2$). CO_2 capture at this scale is needed to establish the reliability and environmental performance of different types of power systems with capture, to reduce costs of CCS, and improve confidence in the estimates. In addition, large-scale implementation is needed to obtain better estimates of the costs and performance of industrial processes such as the cement and steel industries that are significant sources of CO_2, but have little or no experience with CO_2 capture

With regard to mineral carbonation technology, a major question is how to exploit the reaction heat in practical designs that can reduce costs and net energy requirements. Experimental facilities at pilot scales are needed to address these gaps.

With regard to industrial energy use, further study of the net energy and CO_2 performance of industrial facilities that use captured CO_2 can help to get a more complete picture of the potential of this option.

Location, costs and number of CO_2 sources

Improving knowledge of the proximity of major CO_2 sources to suitable storage sites (of all types), as well as establishing cost curves for capture, transport and storage of CO_2, would facilitate decision-making on large-scale deployment of CCS. In this context, detailed regional assessments are required to evaluate how well large CO_2 emission sources (both current and future) match with suitable storage options that can store the volumes required.

Geological storage capacity and effectiveness

There is a need for improved storage capacity estimates at the global, regional and local levels, and better knowledge of very long term storage, migration and leakage processes. Addressing the latter issue will require an enhanced ability to monitor and verify the behaviour of geologically stored CO_2. Implementation of more pilot and demonstration storage projects in a range of geological,

geographical and economic settings would be important to improve the understanding of these issues.

Impacts of ocean storage

Major knowledge gaps that should be filled before the risks and potential for ocean storage can be assessed, concern the ecological impacts of CO_2 in the deep ocean. Studies are needed of the response of biological systems in the deep sea to added CO_2, including studies that are longer in duration and larger in scale than yet performed. Coupled with this is a need to develop techniques and sensors to detect and monitor CO_2 plumes and their biological and geochemical consequences.

Legal and regulatory issues

There is currently inadequate knowledge concerning the legal and regulatory requirements for implementing CCS on a larger scale. An appropriate framework is lacking that would be needed to facilitate the implementation of geological storage, and which would take into account the associated long-term liabilities. Clarification is needed regarding potential legal, environmental, or other constraints on the use of ocean storage. Other key knowledge gaps are related to the methodologies for emissions inventories and accounting.

Global contribution of CCS to mitigating climate change

There are several other issues that would help future decision making on CCS by further improving our understanding of the potential contribution of CCS to long-term global mitigation and stabilization of greenhouse gas concentrations. These include the potential for transfer and diffusion of CCS technologies, including opportunities for developing countries to exploit CCS, application to biomass sources of CO_2, and the potential interaction between investment in CCS and other mitigation options. Further investigation is warranted of the question of how long CO_2 would need to be stored, which is related to stabilization pathways and intergenerational aspects.

the growth in emissions into the future; however, on their own, efficiency gains are unlikely to be sufficient and economically feasible to achieve deep reductions in emissions of GHGs (IPCC, 2001a).

1.3.2 Switch to less carbon-intensive fossil fuels

Switching from high carbon to low carbon fuels can be cost-effective today where suitable supplies of natural gas are available. Typical emission reduction is 420 kg CO_2/MWh for the change from coal to gas in electricity generation, i.e. about 50% (IPCC, 1996b). If coupled with the introduction of combined production of heat, cooling and electric power, the reduction in emissions would be even greater. This would make a substantial contribution to emissions reduction from a particular plant but is restricted to plant where supplies of lower carbon fuels would be available.

1.3.3 Increased use of low and near zero-carbon energy sources

Deep reductions in emissions from stationary sources could be achieved by widespread switching to renewable energy or nuclear power (IPCC, 2001a). The extent to which nuclear power could be applied and the speed at which its use might be increased will be determined by that industry's ability to address concerns about cost, safety, long term storage of nuclear wastes, proliferation and terrorism. Thus its role is likely to be determined more by the political process and public opinion than by technical factors (IPCC, 2001a).

There is a wide variety of renewable supplies potentially available – commercial ones include wind, solar, biomass, hydro, geothermal and tidal power, depending on geographic location. Many of them could make significant contributions to electricity generation, as well as to vehicle fuelling and space heating or cooling, thereby displacing fossil fuels (IPCC, 2001a). Many of the renewable sources face constraints related to cost, intermittency of supply, land-use and other environmental impacts. Between 1992 and 2002, installed wind power generation capacity grew at a rate of circa 30% per year, reaching over 31 GW_e by the end of 2002 (Gipe, 2004). Solar electricity generation has increased rapidly (c. 30% per year), achieving 1.1 GW_e capacity in 2001, mainly in small-scale installations (World Energy Assessment, 2004). This has occurred because of falling costs as well as promotional policies in some countries. Liquid fuel derived from biomass has also expanded considerably and is attracting the attention of several countries, e.g. Brazil, due to its declining costs and co-benefits in creation of jobs for rural populations. Biomass used for electricity generation is growing at about 2.5% per annum; capacity had reached 40 GWe in 2001. Biomass used for heat was estimated to have capacity of 210 GW_{th} in 2001. Geothermal energy used for electricity is also growing in both developed and developing countries, with capacity of 3 GW_e in 2001 (World Energy Assessment, 2004). Thus, there are many options which could make deep reductions by substituting for fossil fuels, although the cost is significant for some and the potential varies from place to place (IPCC, 2001a).

1.3.4 Sequester CO_2 through the enhancement of natural, biological sinks

Natural sinks for CO_2 already play a significant role in determining the concentration of CO_2 in the atmosphere. They may be enhanced to take up carbon from the atmosphere. Examples of natural sinks that might be used for this purpose include forests and soils (IPCC, 2000b). Enhancing these sinks through agricultural and forestry practices could significantly improve their storage capacity but this may be limited by land-use practice, and social or environmental factors. Carbon stored biologically already includes large quantities of emitted CO_2 but may not be permanent.

1.3.5 Capture and storage of CO_2

As explained above, this approach involves the capture of CO_2 from combustion of fuels, or released from industrial processes, and then storing it away from the atmosphere for a very long time. In the Third Assessment Report (IPCC, 2001a) this option was analyzed on the basis of a few, documented projects (e.g. the Sleipner Vest gas project in Norway, enhanced oil recovery practices in Canada and USA, enhanced recovery of coal bed methane in New Mexico and Canada). That analysis also discussed the large potential of fossil fuel reserves and resources, as well as the large capacity for CO_2 storage in depleted oil and gas fields, deep saline formations, and in the ocean. It also pointed out that CO_2 capture and storage is more appropriate for large sources, such as central power stations, refineries, ammonia, and iron and steel plants, than small, dispersed emission sources.

The contribution that this technology could make will be influenced by factors such as the cost relative to other options, the time that CO_2 will remain stored, the means of transportation to storage sites, environmental concerns, and the acceptability of this approach. The CCS process requires additional fuel and associated CO_2 emissions compared with a similar plant without capture.

Recently it has been recognized that biomass energy used with CO_2 capture and storage (BECS) can yield net removal of CO_2 from the atmosphere because the CO_2 put into storage comes from biomass which has absorbed CO_2 from the atmosphere as it grew (Möllersten *et al.*, 2003; Azar *et al.*, 2003). The overall effect is referred to as "negative net emissions". BECS is a new concept that has received little analysis in technical literature and policy discussions to date.

1.3.6 Potential for reducing CO_2 emissions

It has been determined (IPCC, 2001a) that the worldwide potential for GHG emission reduction by use of technological options such as those described above amounts to between 6950 and 9500 $MtCO_2$/y (1900 to 2600 MtC/yr) by 2010, equivalent to about 25 to 40% of global emissions respectively. The potential rises to 13,200 to 18,500 $MtCO_2$/yr (3,600 to 5,050 MtC/yr) by 2020. The evidence on which these estimates are based is extensive but has several limitations - for instance, the data used comes from the 1990s and additional new technologies have since emerged. In addition, no comprehensive worldwide study of technological and economic potential has yet been performed; regional and national studies generally have had different scopes and made different assumptions about key parameters (IPCC, 2001a).

The Third Assessment Report found that the option for reducing emissions which had the largest potential in the short-term (up to 2020) was energy efficiency improvement while the near-term potential for CO_2 capture and storage was considered modest, amounting to 73 to 183 $MtCO_2$/yr (20 to 50 MtC/yr) from coal and a similar amount from natural gas (see Table TS.1 in IPCC, 2001a). Nevertheless, faced with the longer-term climate challenge described above, and in view of the growing interest in this option, it has become important to analyze the potential of this technology in more depth.

As a result of the 2002 IPCC workshop on CO_2 capture and storage (IPCC, 2002), it is now recognized that the amount of CO_2 emissions which potentially could be captured and stored may be higher than the value given in Third Assessment Report. Indeed the emissions reduction may be very significant compared with the values quoted above for the period after 2020. Although wider use of this option may tend to restrict the opportunity to use other supply options, nevertheless such action might still lead to an increase in emissions abatement because much of the potential estimated previously (IPCC, 2001a) was from application of measures concerned with end-uses of energy. Some applications of CCS are relatively low cost (for example, storage of CO_2 from gas

processing as is done in the Sleipner project (Baklid *et al.*, 1996) which might allow their use at a relatively early date. Certain large industrial sources could present interesting low-cost opportunities for CCS, especially if combined with storage opportunities which generate compensating revenue, such as CO_2 Enhanced Oil Recovery (IEA GHG, 2002) - this is discussed in Chapter 2.

1.3.7 Comparing mitigation options

There is a variety of factors which will need to be taken into account in any comparison of mitigation options, not least who is making the comparison and for what purpose. The remainder of this chapter discusses various aspects of CCS in a context which may be relevant to decision makers. In addition there are broader issues, especially questions of comparison with other mitigation measures. Answering such questions will depend on many factors, including the potential of each option to deliver emissions reductions, available national resources, accessibility of each technology to the country concerned, national commitments to reduce emissions, the availability of finance, public acceptance, likely infrastructural changes, environmental side-effects, etc. Most such aspects must be considered both in relative terms (e.g. how does this compare with other mitigation options?) and absolute terms (e.g. how much does this cost?), some of which will change over time as the technology advances.

The IPCC (2001a) found that improvements in energy efficiency have the potential to reduce global CO_2 emissions by 30% below year 2000 levels using existing technologies, for costs of less than \$30/t CO_2 (\$100/t C). Half of this reduction could be achieved with existing technology at zero or net negative costs[9]. Wider use of renewable energy sources was also seen to have substantial potential. Carbon sequestration by forests was considered a promising near-term mitigation option (IPCC, 2000b), attracting commercial attention at prices of \$0.8 to \$1.1/tCO_2 (\$3 to 4/tC) although. The costs quoted for mitigation in most afforestation projects are presented on a different basis from the way in which power generation options are presented, making the afforestation examples look more favourable (Freund and Davison, 2002). Nevertheless, even after allowing for this, the cost of current projects is low.

It is important in comparing different mitigation options to consider not just costs but also the potential capacity for emission reduction. A convenient way of doing this is to use Marginal Abatement Cost-curves (MACs) to describe the potential capacity for mitigation - these are not yet available for all mitigation options but are being developed (for example see IEA GHG, 2000b). Several other aspects of the comparison of mitigation options are discussed later in this chapter and in Chapter 8.

1.4 Characteristics of CO_2 capture and storage

In order to help the reader understand how CO_2 Capture and Storage could be used as a mitigation option, some of the key features of the technology are briefly introduced here.

1.4.1 Overview of the CO_2 capture and storage concept and its development

Capturing CO_2 typically involves separating it from a gas stream. Suitable techniques were developed 60 years ago in connection with the production of town gas; these involved scrubbing the gas stream with a chemical solvent (Siddique, 1990). Subsequently they were adapted for related purposes, such as capturing CO_2 from the flue gas streams of coal or gas burning plant for

[9] Meaning that the value of energy savings would exceed the technology capital and operating costs within a defined period of time using appropriate discount rates.

carbonation of drinks and brine, and for enhancing oil recovery. These developments required improving the process so as to inhibit the oxidation of the solvent in the flue gas stream. Other types of solvent and other methods of separation have been developed more recently. This technique is widely used today for separating CO_2 and other acid gases from natural gas streams[10]. Application of this type of technology to mitigation of climate change was first discussed by Horn and Steinberg (1982) and by Hendriks *et al.* (1989) among others, with initial focus on electricity generation. CO_2 removal is already used in the production of hydrogen from fossil fuels; application of capture and storage in this process as a climate protection measure was discussed by Audus *et al.* (1996).

In order to transport CO_2 to possible storage sites, it is compressed to reduce its volume – in its so-called dense phase, CO_2 occupies around 0.2% of the volume of the gas at standard temperature and pressure (see Appendix 1 for further information on properties of CO_2). Several million tonnes/year of CO_2 are transported today by pipeline (Skovholt, 1993), by ship and by road tanker.

For storage of CO_2, many options are, in principle, available. The first proposal of such a concept (Marchetti, 1977) envisaged injection of CO_2 into the ocean so that it was carried into deep water where, it was thought, it would remain for hundreds of years. In order to make a significant difference to the atmospheric loading of greenhouse gases, the amount of CO_2 that would need to be stored in this way would have to be significant compared to the amounts of CO_2 currently emitted to the atmosphere – in other words Gt of CO_2/year. The only potential storage sites with capacity for such quantities are natural reservoirs, such as geological formations (the capacity of European formations was first assessed by Holloway *et al.*, 1996) or the deep ocean (Cole *et al.*, 1993). Other storage options have also been proposed, as discussed below.

Injection of CO_2 underground would involve similar technology to that employed by the oil and gas industry for exploration and production of hydrocarbons, and for the underground injection of waste as practiced in the USA. Wells would be drilled into geological formations and CO_2 would be injected in the same way as CO_2 has been injected for enhanced oil recovery[11] since the 1970s (Blunt *et al.*, 1993; Stevens and Gale, 2000). In some cases, this could lead to enhanced production of hydrocarbons, which would help to offset the cost. An extension of this idea involves injection into saline formations (Koide *et al.*, 1992) or into unminable coal seams (Gunter *et al.*, 1997) - in the latter case, such injection may sometimes result in displacement of methane which could be used as a fuel. The world's first commercial scale CO_2 storage facility, which began operation in 1996, makes use of a deep saline formation under the North Sea (Korbol and Kaddour, 1995; Baklid *et al.*, 1996).

Monitoring will be required both for purposes of management of the storage site and to verify the extent of CO_2 emissions reduction which has been achieved. Techniques such as seismic surveys, developed by the oil and gas industry, have been demonstrated as being able to observe CO_2 underground (Gale *et al.*, 2001) and may form the basis for monitoring of CO_2 stored in such reservoirs.

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[10] The total number of installations is not known but is probably several thousand. Kohl and Nielsen (1997) mention 334 installations using physical solvent scrubbing; this source does not provide a total for the number of chemical solvent plant but they do mention one survey which alone examined 294 amine scrubbing plants. There is also a number of membrane units and other methods of acid gas treatment in use today.

[11] For example in 2002 there were 40 gas processing plants in Canada where CO_2 and H_2S are separated from produced natural gas and injected into geological reservoirs (see Chapter 5.2.4). There are also 76 Enhanced Oil Recovery projects where CO_2 is injected underground (Stevens and Gale, 2000).

Many alternatives to storage of dense phase CO_2 have been proposed - for example, using the CO_2 to make chemicals or other products (Aresta, 1987), fixing it in mineral carbonates for storage in a solid form (Seifritz, 1990; Dunsmore, 1992), storing it as solid CO_2 ("dry ice") (Seifritz, 1992), as CO_2 hydrate (Uchida *et al.*, 1995), or as solid carbon (Steinberg, 1996). Another proposal is to capture the CO_2 from flue gases using micro-algae to make a product which can be turned into a biofuel (Benemann, 1993).

The potential role for capture and storage of CO_2 as a mitigation option has to be examined through use of integrated energy system models (early studies by Yamaji (1997) have subsequently been followed by many others). An assessment of the environmental impact of the technology through life cycle analysis was reported by Audus and Freund (1997) and other studies have since examined this further.

Thus the concept of capture and storage of CO_2 is based on a combination of known technologies applied to the new purpose of mitigating climate change. The economic potential for this technique to enable deep reductions in emissions was examined by Edmonds *et al.* (2001), and is discussed in more detail in Chapter 8. The scope for further improvement of the technology and for development of new ideas is examined in later chapters, each of which focuses on a specific part of the system.

1.4.2 Systems for capture of CO_2

Figure 1.3 illustrates how CO_2 capture and storage may be configured for use in electricity generation. A conventional fossil fuel-fired power plant is shown schematically in Figure 1.3a - in this the fuel, for example natural gas, and an oxidant, typically air, are brought together in a combustion system; heat from this is used to drive a turbine/generator which produces electricity. The exhaust gases are released to atmosphere.

Figure 1.3. a) Schematic diagram of fossil fuel based power generation; b) Schematic diagram of Post-combustion capture; c) Schematic diagram of Pre-combustion capture; d) Schematic diagram of Oxyfuel combustion

Figure 1.3b shows such a plant modified to capture CO_2 from the flue gas stream, in other words after combustion. Once it has been captured, the CO_2 is compressed in order to transport it to the storage site. Figure 1.3c shows another variant where CO_2 is removed before combustion (pre-combustion decarbonisation). Figure 1.3d represents an alternative where nitrogen is extracted from air before combustion - in other words, pure oxygen is supplied as the oxidant. This type of system is commonly referred to as oxyfuel combustion; a necessary part of this process is the recycle of CO_2 or water to moderate the combustion temperature.

1.4.3 Range of possible uses

The main application examined, so far, for capture and storage of CO_2 is in power generation. However, in other large energy-intensive industries (e.g. cement manufacture, oil refining, ammonia production and iron and steel manufacture), individual plants can also emit large amounts of CO_2, so these industries also have the potential to make use of this technology. In some cases, for example production of ammonia or hydrogen, the nature of the exhaust gases (being concentrated in CO_2) would make separation less expensive.

Thus, the main applications foreseen for this technology are in large, central facilities that produce significant quantities of CO_2. However, as indicated in Table 1.1, roughly 38% of emissions arise from dispersed sources such as buildings and, especially, vehicles. These are generally not considered suitable for direct application of CO_2 capture because of the economies of scale

associated with the capture processes as well as the difficulties and costs of transporting small amount of CO_2. An alternative approach would be to reduce the emissions from dispersed sources by supplying them with an energy carrier which has zero net CO_2 emissions from use, such as biofuels, electricity or hydrogen (Johansson *et al.*, 1993). Production of electricity or hydrogen[12] from fossil fuels could be done with CO_2 capture and thus avoid most of the CO_2 emissions at the production site (Audus *et al.*, 1996). The cost, applicability and environmental aspects of various applications are discussed later in this report.

1.4.4 Scale of the plant

Some impression of the scale of the plant involved can be gained from considering a coal-fired power plant generating 500MW_e. This would emit approximately 2.9 Mt CO_2/yr (0.8 Mt C/yr) to atmosphere. A comparable plant with capture and storage of CO_2, producing a similar amount of electricity as well as capturing 85% of the CO_2 (after combustion) and compressing it for transportation, would emit 0.6 MtCO_2/yr to the atmosphere (0.16 MtC/yr) – in other words 80% less than in the case without capture. The latter plant would also send 3.4 MtCO_2/yr to storage (0.9 MtC/yr). Because of its larger size, the amount of CO_2 generated by the plant with capture and compression is more than the plant without capture (in this example 38% more). This is a result of the energy requirements of the capture plant and of the CO_2 compressor. The proportion of CO_2 captured (85%) is a level readily achievable with current technology - this is discussed in Chapter 3; it is certainly feasible to capture a higher proportion and designs will vary from case to case. These figures demonstrate the scale of the operation of a CO_2 capture plant and illustrate that capturing CO_2 could achieve deep reductions in emissions from individual power plants and similar installations (IEA GHG, 2000a).

Given a plant of this scale, the quantities of CO_2 could be handled by a pipeline of 300-400mm diameter over distances of hundreds of kilometres without further compression; for longer distances extra compression might be required to maintain pressure. Larger pipelines could carry the CO_2 from several plants over longer distances at lower unit cost. Storage of CO_2, for example by injection into a geological formation, would likely involve several million tonnes of CO_2/year but the precise amount will vary from site to site as discussed in Chapters 5 and 6.

1.5 Assessing CCS in respect of environmental impact and cost

The purpose of this and the following sections is to introduce some of the other issues potentially of interest to decision-makers when considering CCS. Answers to some of the questions posed may be found in subsequent chapters although answers to others will depend on further work and local information. In considering the use of CCS, important considerations will include the environmental and resource implications, as well as the cost. A systematic process of evaluation is needed which can examine all the stages of the CCS system in these respects and can be used for this and other mitigation options. A well-established method of analyzing environmental impacts in a systematic manner is the technique of Life Cycle Analysis (LCA). This is codified in the International Standard ISO 14040 (ISO, 1997). First it is necessary to establish a system boundary, and then to compare the system with CCS to a base-case (reference system) without CCS. The difference will define the environmental impact of CCS. A similar approach enables systematic assessment of the resource and/or cost implications of CCS.

[12] Production of hydrogen from fossil fuels is done today in oil refineries and other industrial processes.

1.5.1 Establishing a system boundary

A generic system boundary is shown in Figure 1.4, along with the flows of materials into and out of the system. The key flow[13] is the product stream, which may be an energy product (such as electricity or heat), or other product with economic value such as hydrogen, cement, chemicals, fuels or other goods. In analyzing the environmental and resource implications of CCS, the convention used throughout this report is to normalize all of the system inputs and outputs to a unit quantity of product e.g. electricity. As explained later, this concept is essential for establishing the effectiveness of this option - in this particular case, the total amount of CO_2 produced is increased due to the additional equipment and operation of the CCS plant. In contrast, a simple parameter, such as the amount of CO_2 captured, may be misleading.

Inputs to the process include the fossil fuels used to meet process energy requirements, as well as other materials used by the process (such as water, air, chemicals, or biomass used as a feedstock or energy source). These may involve renewable or non-renewable resources. Outputs to the environment include the CO_2 stored and emitted, plus any other gaseous, liquid or solid emissions released to the atmosphere, water or land. Changes in other emissions, not just CO_2, may also be important. Other aspects which may be relatively unique to CCS include the ability to keep the CO_2 separate from the atmosphere and the possibility of unpredictable effects, for example the consequences of climate change, but these are not quantifiable in an LCA.

Use of this procedure would enable robust comparison of different CCS options. In order to compare an electric power plant with CCS with other ways of reducing CO_2 emissions from electricity production, e.g. use of renewable energy, a broader system boundary may have to be considered.

Figure 1.4. System boundary for a plant or process emitting CO_2 (such as a power plant, a hydrogen production plant or other industrial process). The resource and environmental impacts of a CCS system are measured by the changes in total system input and output quantities needed to produce a unit of product.

1.5.2 Application to assessing environmental and resource impacts

The three main components of the CO_2 capture, transport and storage system are illustrated in Figure 1.5 as sub-systems within the overall system boundary - for an electric power plant with CCS. As a result of the additional requirements for operating the CCS equipment, the quantity of fuel and other material inputs needed to produce a unit of product (e.g. one MWh of electricity) is increased relative to the base case without CCS and there will also be increases in some emissions and reductions in others. Specific details of the CCS sub-systems illustrated in Figure 1.5 are presented in Chapters 3-7, along with the quantification of CCS energy requirements, resource requirements and emissions.

Figure 1.5. System components inside the boundary of Figure 1.4 for the case of a power plant with CO_2 capture and storage. Solid arrows denote mass flows while dashed lines denote energy flows. The magnitude of each flow depends upon the type and design of each sub-system, so only some of the flows will be present or significant in any particular case. To compare a plant with CCS with another system having similar product, e.g. a renewables-based power plant, a broader system boundary may have to be used.

[13] Referred to as the “elementary flow” in life cycle analysis.

1.5.3 Application to assessing cost

The cost of capture and storage of CO_2 is typically built up from 3 separate components – the cost of capture (including compression), the cost of transportation and the cost of storage (including cost of monitoring and, if necessary, remediation of any release). Any income from EOR (if applicable) would help to partially offset the cost as would credits from an emissions trading system or from avoiding a carbon tax if those were introduced. The costs of individual components are discussed in Chapters 3 to 7; the costs of whole systems and alternative options are considered in Chapter 8. The confidence levels of cost estimates for technologies at different stages of development and commercialization are also discussed in those chapters.

There are various ways of expressing the cost data (Freund and Davison, 2002). One convention is to express the costs in terms of US$/t$CO_2$ avoided, which has the important feature of taking into account the additional energy (and emissions) resulting from capturing the CO_2. This is very important for understanding the full effects on the particular plant of capturing CO_2, especially the increased use of energy. However, as a means of comparing mitigation options, this can be confusing since the answer depends on the base-case chosen for the comparison (i.e. what is being avoided). Hence, for comparison with other ways of supplying energy or services, the cost of systems with and without capture are best presented in terms of a unit of product, e.g. the cost of generation (e.g. US$/MWh) coupled with the CO_2 emissions per unit of electricity generated (e.g. tCO_2/MWh). Then the user can choose the appropriate base-case best suited to their purposes. This is the approach used in this report and is consistent with the treatment of environmental implications described above.

Expressing the cost of mitigation in terms of US$/t$CO_2$ avoided is also used when considering mitigation options for a *collection* of plants (such as a national electricity system). This is typically found in integrated assessment modelling done for policy-related purposes (see Chapter 8). The costs calculated in that way should not be compared with the cost of CO_2-avoided calculated for an *individual* power plant of a particular design as described above because the base-case will not be the same. However, because the term “avoided” is used in both cases, there can be misunderstanding if a clear distinction is not made.

1.5.4 Other aspects of cost and environmental impact

Most of the published studies of specific projects consider particular CO_2 sources and particular storage reservoirs. Necessarily these use costs appropriate to particular plant, so that the quantities of CO_2 involved are typically only a few million tonnes per year. Although these are realistic quantities for the first such projects, they fail to reflect the potential economies of scale which are likely to be found if/when this technology is widely used for mitigation of climate change. Under those circumstances, much greater quantities of CO_2 would have to be captured, transported and stored. It can be expected that, over a period of several decades, there would be reductions in costs as a result of both economies of scale and increased experience in the manufacture and operation of most stages of the CCS system. Such effects of “learning” have been seen in many technologies, including energy technologies, although historically observed rates of improvement and cost reduction are quite variable and have not been accurately predicted for any specific technology (McDonald and Schrattenholzer, 2001).

Construction of any large plant will present issues of environmental impact, which is why impact analyses are required in many countries before approval of such projects. There will probably be a requirement for gaining a permit for the work. Chapters 3 to 7 discuss in more detail the environmental issues and impacts associated with CO_2 capture, transport and storage. At a power plant, those impacts will depend largely on the type of capture system employed and the extra

energy required, which would increase the flows of fuel and chemical reagents and some of the emissions associated with generating a kilowatt-hour of electricity. Construction and operation of CO_2 pipelines will have similar impact on the environment as natural gas pipelines currently do. Large-scale transportation and storage of CO_2 also has the potential, if significant amounts were to escape, to create a potential hazard (see Appendix 1).

The different storage options may carry differing obligations in respect of monitoring and liability. Monitoring of CO_2 flows will take place at all parts of the system for reasons of process control. It will also be necessary to monitor the systems to ensure that the storage is safe and secure, to provide data for national inventories and to provide a basis for CO_2 emissions trading.

In developing monitoring strategies, especially for reasons of regulatory compliance and verification, a key question concerns how long the monitoring must continue – clearly monitoring will be needed throughout the injection phase but the frequency and extent of monitoring after injection has been completed still needs to be determined, and the organisation(s) responsible for monitoring in the long term will have to be identified. Also, in cases where CO_2 is put to use, for example for enhanced oil recovery, it will be necessary to establish the net-amount of CO_2 stored. The extent to which the guidelines for reporting emissions already developed by IPCC need to be adapted for this new mitigation option is discussed in Chapter 9.

In order to help understand the nature of the risks, a distinction may usefully be drawn between slow seepage of CO_2 and larger, unintended releases arising from rapid failure of some part of the system, which could be potentially hazardous (see Appendix 1 for information on the danger that CO_2 can present in certain circumstances). CO_2 disperses readily in turbulent air but seepage from stores under land might have noticeable effects on local ecosystems depending on the amount released and the size of the area affected. If under the sea, any CO_2 dissolved in seawater would be quickly dispersed by marine currents. CO_2 seeping from a storage reservoir may intercept shallow aquifers or surface water bodies - if these supplied potable water, this could have direct consequences for human activity. There is considerable uncertainty over the potential local ecosystem damage that could arise from seepage of CO_2 from underground reservoirs – small seepages may produce no detectable impact although it is known that measurable damage occurs from relatively large releases from natural CO_2 reservoirs (Sorey *et al.*, 1996). However, if the cumulative amount released from purposeful storage was significant, this could have an impact on the climate. In that case, this would need to be allowed for in national inventories (as discussed in Chapter 9). The likely level of seepage from geological storage reservoirs is the subject of current research which is described in Chapter 5. Such environmental considerations form the basis for some of the legal barriers to storage of CO_2 which are discussed in Chapters 5 and 6.

The environmental impact of CCS, as with any other energy system, can be expressed as an external cost (IPCC, 2001d) but relatively little has been done to apply this approach to CCS and so it is not discussed further in this report. The results of an application of this approach to CCS can be found in Audus and Freund (1997).

1.6 Assessing CCS in respect of energy supply and CO_2 storage

Among the first questions raised when the subject of carbon dioxide capture and storage is mentioned are:

- Are there enough fossil fuels to make this worthwhile?
- How long will the CO_2 remain in store?
- Is there sufficient storage capacity and how widely is it available?

These questions are closely related to the minimum time it is necessary to keep CO_2 out of the atmosphere in order to mitigate climate change, which is exemplified by a fourth question "How long does the CO_2 need to remain in store?" An approach to answering these questions is indicated below. Finally, broader issues relating to fossil fuels and other scenarios are briefly discussed.

1.6.1 Fossil fuel availability

Fossil fuels are globally traded commodities that are available to all countries and potentially could be used for much of the 21st century although the balance amongst the different fuels may change. Capture and storage of CO_2 would enable countries, if they wish, to continue to include fossil fuels in their energy mix, even with severe restrictions on greenhouse gas emissions.

Whether fossil fuels will last long enough to justify the development and large-scale deployment of capture and storage of CO_2 depends on a number of factors, including their depletion rate, cost, and the composition of the fossil fuel resources and reserves.

1.6.1.1 Depletion rate and cost of use

Proven coal, oil and natural gas reserves are finite so consumption of these primary fuels can be expected to peak and then decline at some time in the future (IPCC, 2001a). However, predicting the pace at which use of fossil fuels will fall is far from simple because of the multiplicity of different influences. Alternative sources of energy are being developed which will compete with fossil fuels, thereby extending the life of the reserves. Extracting fossil fuels from more difficult locations will increase the cost of supply, as will the use of feedstocks that require greater amounts of processing; the resultant increase in cost will also tend to reduce demand. Restrictions on emissions, whether by imposition of a cap or of a tax, would also increase the cost of using fossil fuels, as would application of CCS. At the same time, improved technology will reduce the cost of using them. All but the last of these factors will have the effect of extending the life of the reserves of fossil fuels, although application of CCS would tend to increase the demand for them.

1.6.1.2 Reserves and resources of fossil fuels

On top of the known reserves there are significant resources that, through technology advances and the willingness of society to pay more for them, may be converted into commercial fuels in the future. Furthermore, there are thought to be large amounts of non-conventional oil (e.g. heavy oil, tars sands, shales) and gas (e.g. methane hydrates). A quantification of these in the Third Assessment Report (IPCC, 2001a) showed that fully exploiting the known oil and natural gas resources (without any emission control) plus use of non-conventional resources would cause the atmospheric concentrations of CO_2 to rise to a level above 750 ppmv. In addition, coal resources are even larger than those of oil and gas; consuming all of them would enable the global economy to emit 5 times as much CO_2 as has been released since 1850 (5,200 $GtCO_2$ or 1,500 GtC) (see chapter 3 in IPCC, 2001a). A scenario for achieving significant reductions in emissions (Berk *et al.*, 2001) demonstrates the extent to which a shift away from fossil fuels would be required to stabilize at 450 ppmv by 2100 but without the use of CCS. Thus, sufficient fossil fuels exist for decades more use so that the availability of fossil fuels does not put a limit on the potential application of CO_2 capture and storage but CCS would provide a way of limiting the environmental impact of the continued use of fossil fuels.

1.6.2 Is there sufficient storage capacity?

To achieve stabilization at 550ppmv, the Third Assessment Report (IPCC, 2001e) showed that, by 2100, the reduction in emissions could be around 38 $GtCO_2$/yr (10GtC/yr)[14] compared with scenarios with no mitigation action. If CO_2 capture and storage is to make a significant contribution towards reducing emissions, it could be expected that several hundreds to thousands of plants would need to be built, each capturing 1 to 5 $MtCO_2$/yr (0.27-1.4MtC/yr). The magnitudes of these figures are consistent with the numbers of plants that are built and operated by electricity companies and other manufacturing enterprises.

Initial estimates of the capacity of known storage reservoirs (IEA GHG, 2001; IPCC, 2001a) indicate these are comparable in capacity with the amount of CO_2 which would be produced for storage by such plants. More recent estimates are given in Chapters 5 and 6, although differences in methods of estimating storage capacity demonstrate the uncertainties in these estimates – such issues are discussed in later chapters. Storage other than in natural reservoirs, which might be artificial stores or by changing CO_2 into another form (Freund, 2001), generally does not offer similar capacity for abatement of emissions with low costs (Audus and Oonk, 1997) - some aspects of this are discussed further in Chapter 7.

The extent to which these reservoirs are within reasonable, cost competitive distance of the sources of CO_2 will determine the potential for using this mitigation option.

1.6.3 How long will the CO_2 remain in storage?

This seemingly simple question is, in fact, a surprisingly complicated one to answer since the mechanisms and rates of release are quite different for different options. In this report, we use the term "fraction retained" to indicate how much CO_2 remains in store for how long. The definition is as follows:

- "*Fraction retained*" is the fraction of the cumulative amount of injected CO_2 that is retained in the storage reservoir over a specified period of time, e.g. a hundred or a million years.

Chapters 5, 6 and 7 provide more information for particular classes of store. The above definition makes no judgement about how the amount of CO_2 retained in storage will evolve over time - if there were to be an escape of CO_2, it may not be at a uniform rate.

The CO_2 storage process and its relationship to concentrations in the atmosphere can be understood by considering the stocks of stored CO_2 and the flows between reservoirs - Figure 1.6 is a schematic diagram that shows the major stocks in natural and potential engineered storage reservoirs, and the flows to and from them. Under current patterns of fossil fuel use, CO_2 is released directly to the atmosphere from human sources. The amount of CO_2 released into the atmosphere by combustion and industrial processes can be reduced by a combination of the various mitigation measures described above. These flows are shown as alternative pathways in Figure 1.6.

Figure 1.6. Schematic diagram of stocks and flows of CO_2 with net flows of captured CO_2 to each reservoir indicated by the label CCS (these flows exclude residual emissions associated with the process of capture and storage). The release flows from each of the storage reservoirs are indicated by the labels R. The stock in the atmosphere depends upon the difference between the rates at

[14] This is an indicative value calculated by averaging the figures across the 6 SRES marker scenarios; there is considerable variation in this value depending on scenario and the parameter values used in the climate model.

which CO_2 reaches the atmosphere and at which it is removed. Flows to the atmosphere may be slowed by a combination of mitigation options, such as improving energy efficiency or use of alternatives to fossil fuels, by enhancing biological storage or by utilizing CCS in geological formations, in the oceans or in chemicals or minerals.

The flows marked ***CCS*** with a subscript are the *net* tons of carbon dioxide per year that can potentially be placed into each of the three types of storage reservoir considered in this report. Additional emissions associated with the capture and storage process are not explicitly indicated but may be considered as additional sources of CO_2 emission to the atmosphere. The potential release flows from the reservoirs to the atmosphere are indicated by ***R*** with a subscript indicating the appropriate reservoir. For some of the storage options the release flows can be very small compared with the flows into those storage reservoirs.

The *amount* in storage at a particular time is determined by the capacity of the reservoir and the past history of additions to and releases from the reservoir. The *change* in stocks of CO_2 in a particular storage reservoir over a specified time is determined by the current stock and the relative rates at which the gas is being added and released; in the case of ocean storage, the level of CO_2 in the atmosphere will also influence the net rate of release[15]. As long as the *input* storage rate exceeds the *release* rate, CO_2 will accumulate in the reservoir, and some amount will be stored away from the atmosphere. Analysis presented in this report concludes that the timeframes for different storage options cover a wide range:

- The terrestrial biosphere stores and releases both natural and fossil fuel CO_2 through the global carbon cycle. It is difficult to simply convey the fraction retained because of the dynamic nature of this process but typically 99% is stored for decades to centuries although the average lifetime will be towards the lower end of that range. Currently, the terrestrial biosphere is a net sink for carbon dioxide but some current biological sinks are becoming net sources as temperatures rise. The annual storage flows and total carbon storage capacity can be enhanced by forestry and soil management practices. Terrestrial sequestration is not explicitly considered in this report but is covered in IPCC, 2000b.
- Oceans hold the largest amount of mobile CO_2. They absorb and release natural and fossil fuel CO_2 according to the dynamics of the global carbon cycle and with consequent changes in ocean chemistry. The fraction retained by ocean storage at 3,000 m depth could be around 85% after 500 years. However this process has not yet been demonstrated on a significant scale for long periods. Injection at shallower depths would result in shorter retention time. The storage capacity and fractions retained for ocean storage are discussed in Chapter 6.
- In geological storage, insight about the fraction likely to be retained may be gained from observation of natural systems where CO_2 has remained in natural geological reservoirs for millions of years. It may be possible to engineer storage reservoirs that have comparable performance. The fraction retained in appropriately selected and managed geological reservoirs is likely to exceed 99% over 1000 years. However, sudden gas releases from geological reservoirs could be triggered by failure of the storage seal or the injection well, earthquakes or volcanic eruptions, or if the reservoir were accidentally punctured by subsequent drilling activity. Such releases might have significant local effects. Experience from engineered natural gas storage facilities and natural CO_2 reservoirs may be relevant to understanding whether such releases might occur. The storage capacity and fraction retained for the various geological storage options are discussed in Chapter 5.
- Mineral carbonation through chemical reactions would provide a fraction retained of near 100% for exceptionally long times as carbonate rock; however this process has not yet been

[15] For further discussion of this point, see Chapter 6.

demonstrated on a significant scale for long periods and the energy balance may not be favourable. This is discussed in Chapter 7.

- Converting carbon dioxide into other, possibly useful, chemicals may be limited by the energetics of such reactions, the quantities of chemicals produced and their effective lifetimes. In most cases this would result in very small net storage of CO_2. 99% of the carbon will be retained in the product for periods in the order of weeks to months, depending on the product. This is discussed in Chapter 7.

1.6.4 How long does the CO_2 need to remain in storage?

In deciding whether a particular storage option meets mitigation goals, it will be important to know both the net storage capacity and the fraction retained over time. Alternative ways to frame the question are to ask “How long is long enough to achieve a stated policy goal?” or "What is the benefit of isolating a specific amount of CO_2 away from the atmosphere for a hundred or a million years?" The effectiveness of storage includes consideration of factors such as the maximum atmospheric concentration of CO_2 that is set as a policy goal, the timing of that maximum, the anticipated length of the fossil fuel era, and available means of controlling the CO_2 concentration in the event of significant future releases.

The policy relevant issue is whether CO_2 will be held in a particular class of reservoirs sufficiently long that it will not increase the difficulty of meeting future targets for CO_2 concentration in the atmosphere. For example, if 99% of the CO_2 is stored for periods that exceed the projected time span for the use of fossil fuels, this should not to lead to higher concentrations than specified by the policy goal.

One may assess the implications of possible future releases of CO_2 from storage using simulations similar to those developed for generating greenhouse gas stabilization trajectories[16]. Within such a framework one can incorporate a release from storage by counting it as a delayed emission. Some authors examined various ways of valuing unintended releases from storage and determined that a delay in emissions on the order of a thousand years may be almost as effective as perfect storage (IPCC, 2001b; Herzog *et al.*, 2003; Ha-Duong and Keith, 2003)[17]. This applies if marginal carbon prices remain constant or if there is a backstop technology that can cap abatement costs in the not too distant future. However, if discount rates decline in the long term, then less CO_2 must be released from storage in order to achieve the same level of effectiveness.

Other authors propose that the climate impact of CO_2 released from imperfect storage will vary over time, so they expect carbon prices to depend on how the release is accounted for. Haugan and Joos (2004) found that there must be an upper limit to the rate of loss from storage in order to avoid temperature and CO_2 concentration becoming higher in scenarios with geological CCS than in those without it, over the next millennium[18].

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[16] Such a framework attempts to account for the intergenerational trade-offs between climate impacts and the cost of mitigation and aims to choose an emissions trajectory (modified by mitigation measures) that maximizes overall welfare (Wigley *et al.*, 1996; IPCC, 2001a).

[17] For example, Herzog *et al.* (2003) calculated the effectiveness of an ocean storage project relative to permanent storage using economic arguments; for a constant price of carbon, the project would be 97% effective at 3% discount rate; if the price of carbon were to increase at the same rate as the discount rate for 100 years and remain constant thereafter, the project would be 80% effective; for a similar rate of increase but over a 500 year period, the effectiveness would be 45%.

[18] These authors calculated the effectiveness of a storage facility measured in terms of the global warming avoided compared with perfect storage. For a store which annually releases 0.001 of the amount stored, the effectiveness is around 60% after 1000 years. This rate of release would be equivalent to a fraction retained of 90% over 100 years

Dooley and Wise (2003) examined 2 hypothetical scenarios of release using a relatively short 100-year simulation. They showed that relatively high rates of release from store make it impossible to achieve stabilization at levels such as 450 ppmv. They imply that higher emissions trajectories are less sensitive to such releases but, as stabilization is not achieved until later under these circumstances, this result is inconclusive.

Pacala (2003) examined unintended releases using a simulation over several hundred years under an assumption that the security of storage varies amongst the different reservoirs. Although this seemed to suggest quite high release rates could be acceptable, the conclusion depends on extra CO_2 being captured and stored, thereby accumulating in the more secure reservoirs. This would imply that it is important to have reservoirs with low rates of release available for use.

Such perspectives omit potentially important issues such as the political and economic risk that policies will not be implemented perfectly, as well as the resulting ecological risk due to the possibility of non-zero releases which may preclude future stabilization of CO_2 concentrations (Baer, 2003). Nevertheless, all methods imply that, if CO_2 capture and storage is to be acceptable as a mitigation measure, there must be an upper limit to the amount of unintended releases that can take place.

The preceding discussion provides a framework for considering the effectiveness of the retention of CO_2 in storage and suggests a potential context for considering the important policy question: "How long is long enough?" Further discussion of these issues can be found in Chapters 8 and 9.

1.6.5 Timeframe for the technology

Various different timescales are mentioned in discussions of CCS. In this section, we propose some terminology as a basis for the later discussion.

Energy systems, such as power plant and electricity transmission networks, typically have operational lifetimes of 30-40 years; when refurbishment or re-powering is taken into account, the generating station can be supplying electricity for even longer still. Such lifetimes generate expectations which are reflected in the design of the plant and in the rate of return on the investment. The capture equipment could be built and refurbished on a similar cycle, as could the CO_2 transmission system. The operational lifetime of the CO_2 storage reservoir will be determined by its capacity and the timeframe over which it can retain CO_2, which cannot be so easily generalized. However, it is likely that the phase of filling the reservoir will be at least as long as the operational lifetime of a power plant[19]. In terms of protecting the climate, we shall refer to this as **medium-term**, in contrast to the **short-term** nature of measures connected with decisions about operating and maintaining such facilities.

In contrast, mitigation of climate change is determined by longer timescales – for example, the lifetime (or adjustment time) of CO_2 in the atmosphere is often said to be about 100 years (IPCC, 2001c). Expectations for mitigation of climate change typically assume that action will need to be

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or 60% over 500 years. It is likely that, in practice, geological and mineral storage would have lower rates of release than this (see chapters 5 and 7) and hence higher effectiveness – for example, a release rate of 0.01% per year would be equivalent to a fraction retained of 99% over 100 years or 95% over 500 years.

[19] It should be noted that there will not necessarily be a one to one correspondence between CO_2-producing plant and storage reservoir. Given a suitable network for transmission of CO_2, the captured CO_2 from one plant could be stored in different locations during the lifetime of the producing plant.

taken over many decades or centuries (see for example IPCC, 2000a). These will be referred to as **long-term**.

Figure 1.7. The response of atmospheric CO_2 concentrations due to emissions to the atmosphere. Typical values for "near-term", "medium-term", "long-term" and" very long-term" are years, decades, centuries, millennia, respectively. In this example, cumulative emissions are constrained to a maximum value and concentrations stabilise at 550 ppmv (adapted from Kheshgi, 2003). This figure is indicative and should not be read as prescribing specific values for any of these periods. If the goal were to constrain concentrations in the atmosphere to lower levels, such as 450 ppmv, greater reductions in emission rates would be required.

Even so, these descriptors are inadequate for describing the storage of CO_2 as a mitigation measure. As discussed above, it is anticipated that, under virtually all scenarios, CO_2 levels in the atmosphere would rise, peak and decline over a period of several hundred years – this is illustrated in Figure 1.7. If there is effective action for mitigation of climate change, the peak would occur sooner (and be at a lower level) than if no action is taken. As suggested above, most of the CO_2 must be stored for substantially longer than the time required to achieve stabilisation. We recognize this as a **very long term**, indicating centuries to millennia. Precisely how long is a subject of much debate at present and this will be explored in later chapters.

1.6.6 Other effects of introducing CCS into scenarios

In view of the economic importance of energy carriers (more than 2 trillion dollars annually, World Energy Assessment, 2004) as well as fossil fuel's contribution to climate forcing (50 to 60% of the total), the decision to invest economic resources in the development of a technology such as CCS may have deep consequences, including for equity and sustainable development (these are discussed in the following section). This emphasizes the importance of considering the wider ramifications of such investment.

Implementation of CCS would contribute to the preservation of much of the energy infrastructure established in the last century and may help restrain the cost of meeting the target for emissions reduction. From another perspective, its use may reduce the potential for application of alternative energy sources (Edmonds *et al.*, 2001). As noted in section 1.3, mitigation of climate change is a complex issue and it seems likely that any eventual solution will involve a portfolio of methods[20]. Even so, there is concern in some quarters that CO_2 capture and storage option could capture financial resources and the attention of policy makers that would otherwise be filled by alternative measures, although this issue has not been much analyzed in the literature.

The possibility of obtaining net negative emissions when coupling biomass energy and CCS may provide an opportunity to reduce CO_2 concentration in the atmosphere if available on sufficiently large scale. In view of the uncertainty about the safe level of CO_2 concentration in the atmosphere, a large-scale option providing net negative emissions could be especially useful in the context of the precautionary principle.

[20] The optimum portfolio of mitigation measures is likely to be different in different places and at different times. Given the variety of measures available, it seems likely that several will be used in a complementary fashion as part of the portfolio, and there will not be a single clear "winner" amongst them.

1.6.6.1 Effect of CCS on energy supply and use

All of the SRES scenarios (IPCC, 2000a) show significant consumption of fossil fuels for a long time into the future. One of the consequences of deploying CCS would be a continued use of fossil fuels in the energy mix but minimization of their effect on the climate system and environment. By enabling countries to access a wider range of energy supplies than would otherwise be the case, energy security will be improved. Such aspects are important when considering climate change policy and sustainable development - as indicated before, decision makers are likely to balance pure economic effectiveness against other socially relevant issues.

Thus successful development and application of CCS on a large scale might be interpreted by society as a driver for reinforcing socio-economic and behavioural trends that are increasing total energy use, especially in developed countries and within high-income groups in developing countries[21] (IPCC, 2001a).

1.6.6.2 Effect of CCS on technological diversity

The fossil-fuel energy system and its infrastructure can be thought of as a technology cluster. Such a phenomenon can be recognized as possibly presenting dangers as well as offering benefits to society. It can lead to specialization as innovations improve on dominant technologies, thereby generating further innovations which help to retain market share. On the other hand, innovations in technologies with minor market share are less valuable and thus there is less incentive to improve on those technologies, so a minor technology can become trapped in a position of high costs, and a small market share. This phenomenon leads to path dependence or technology lock-in (Bulter and Hofkes, 2004; Unruh, 2000). Although CCS has not yet been examined specifically in this respect, it may be that, by reinforcing the position of the fossil-fuel energy system, this may present barriers to increased technological diversity (a key element in evolutionary change, Nelson and Winter, 1982).

It could be argued that growth in demand for some alternative energy sources will bring significant additional benefits outside the climate change arena such as rural sector jobs, or a large labour force for maintenance (World Energy Assessment, 2004). It is not possible to forecast the full societal impacts of such technology in its early days, especially as it seems likely that stabilizing atmospheric concentrations of CO_2 will require the full slate of available technologies (including ones not yet developed). There is insufficient information available to allow prediction of the differences in job creation potential between different mitigation options.

In view of the paucity of literature on these aspects of CCS, this report cannot provide tools for a full quantitative judgment of options but merely flags some of the other issues that decision makers will wish to consider. This is further discussed in Chapter 8.

1.6.6.3 Financing of the projects

Compared with a similar plant that releases CO_2 to the atmosphere, a facility with capture and storage will cost more to build and to operate and will be less efficient in its use of primary energy. If regulations are adopted which cause the owners of CO_2-emitting plant to limit emissions, and they choose to use CCS (or any other measure which increases their costs), they will need to find ways to recover the extra costs or accept a lower rate of return on their investment. In circumstances

[21] For example, dwelling units in many countries are growing in size, and the intensity of electrical appliance use is increasing. Use of electrical office equipment in commercial buildings is also growing rapidly.

where emissions trading is allowed, companies may, in some cases, reduce the cost of meeting emission targets by purchase or sale of credits. Where the project takes place in another Annex I country, it may be possible to fund this through Joint Implementation (JI). For developing countries, the Clean Development Mechanism (CDM) potentially provides opportunities to acquire technology for emission reduction purposes with some of the costs borne by external funders who can claim credit for these investments. At the time of writing there is uncertainty whether CCS projects would be covered by the CDM and there are many issues to be considered. The current low value of Certified Emission Reductions is a major barrier to such projects at present (IEA GHG, 2004a). It is possible that some CO_2-EOR projects could be more attractive, especially if the project also would delay the abandonment of the field or avoid job losses. The issue of longevity of storage has still to be resolved but the longer retention time for geological formations may make it easier for CCS to be accepted than was the case for natural sinks. A number of countries have potential to host CCS projects involving geological storage under CDM (IEA GHG, 2004a) but the true potential can only be assessed when the underground storage resources have been mapped. The above discussion shows that there are many questions to be answered about the financing of such options, not least if proposed as a project under the flexible mechanisms of the Kyoto Protocol.

1.6.7 Societal requirements

Even if CO_2 capture and storage is cost-effective and can be recognized as potentially fulfilling a useful role in energy supply for a climate-constrained world, there will be other aspects that must be satisfied in order for it to be widely used. For example, what are the legal issues that face this technology? What framework needs to be put in place for long-term regulation? Will CO_2 capture and storage gain public acceptance?

1.6.7.1 Legal issues concerning CCS

Some legal questions about CCS can be identified and answered relatively easily – for example the legal issues relating to the process of capturing CO_2 seem likely to be similar to those facing any large chemical plant. Transportation of CO_2 through pipelines can probably be managed under current regulatory regimes for domestic and international pipelines. The extent to which the CO_2 is contaminated with other substances, such as compounds of sulphur (see Chapter 4), might alter its classification to that of a hazardous substance, subjecting it to more restrictive regulation. However, the storage of carbon dioxide is likely to pose new legal challenges. What licensing procedure will be required by national authorities for storage in underground reservoirs onshore? It seems likely that factors to be considered will include containment criteria, geological stability, potential hazard, possibility of interference with other underground or surface activities and agreement on sub-surface property rights and controls on drilling or mining nearby.

Storage in geological formations below the sea floor will be controlled by different rules from storage under land. The Law of the Sea[22], the London Convention and regional agreements such as the OSPAR Convention[23] will affect storage of CO_2 under the sea but the precise implications have yet to be worked out. This is discussed further in Chapter 5. Ocean storage raises a similar set of questions about the Law of the Sea and the London Convention but the different nature of the activity may generate different responses. These are discussed in Chapter 6.

[22] The full text of these conventions is accessible on the Internet.

[23] Issues of interest for this report are at the time of writing being discussed in the OSPAR convention that regulates the uses of the North East Atlantic.

A further class of legal issues concerns the responsibility for stored carbon dioxide. This is relevant because the CO_2 will have been the subject of a contract for storage, or a contract for emissions reduction, and/or because of the possibility of unintended release. Should society expect private companies to be responsible over centuries for the storage of CO_2? A judgement may have to be made about a reasonable balance between the costs and benefits to current and to future generations. In the case of very long-term storage of nuclear waste, governments have taken on the responsibility for managing the store; the companies that generate the waste, and make a profit from using the nuclear material, pay a fee to the government to take responsibility. In other fields, deep well injection of hazardous materials is sometimes the responsibility of governments and sometimes the responsibility of the companies concerned under a licensing system (IEA GHG, 2004b). Rules about insurance and about liability (if there were to be a release of CO_2) will need to be developed so that, even if something happens in the distant future, when the company that stored it is no longer in business, there will be a means of ensuring another organisation is capable and willing to accept responsibility for it.

The information on legal issues presented in this report reflects the best understanding at the time of writing but should not be taken as definitive as the issues have not been tested.

1.6.7.2 Public acceptance

Only a few studies have been carried out of public attitudes towards CCS. Such research presents challenges because the public is not familiar with the technology, and may only have a limited understanding of climate change and the possibilities for mitigation. As a result the studies completed to date have had to provide information on CCS (and on climate change) to their subjects. This tends to limit the scale of the study which can be carried out. This is described in more detail in Chapter 5.

What form of public consultation will be needed before a CCS project could be approved? Will the public compare CCS with other uses of the underground such as underground storage of natural gas or with nuclear waste disposal? Will they have different concerns about different forms of storage, such as geological or ocean storage of CO_2? Will the general attitude towards building pipelines affect the development of CO_2 pipelines? These and other issues are the subject of current discussion and investigation.

When a CCS project is proposed, the public and governments will want to be satisfied that storage of carbon dioxide is sufficiently secure that, as well as reducing emissions, there will also be no significant threat to human health or to ecosystems (Hawkins, 2003). Monitoring of carbon dioxide transport and storage will be necessary to ensure there is little or no release to the atmosphere but aspects of monitoring are still subject to debate. For example, can the anticipated low rates of CO_2 release from geological storage be detected by currently available monitoring techniques? Who will do this monitoring (IEA GHG, 2004b)? How long should monitoring continue after injection - for periods of decades or centuries (IEA GHG, 2004c)?

1.7 Implications for technology transfer and sustainable development

1.7.1 Equity and sustainable development

The climate change issue involves complex interactions among climatic, environmental, economic, political, institutional, social, scientific, and technological processes. It cannot be addressed in isolation from broader societal goals, such as equity or sustainable development (IPCC, 2001a), or other existing or probable future sources of environmental, economic or social stress. In keeping

with this complexity, a multiplicity of approaches has emerged to analyze climate change and related challenges. Many of these incorporate concerns about development, equity, and sustainability, albeit partially and gradually (IPCC, 2001a).

Sustainable development is too complex a subject for a simple summary – study of this field has the aim of assessing the benefits and trade-offs involved in the pursuit of the multiple goals of environmental conservation, social equity, economic growth, and eradication of poverty (IPCC 2001a, Chapter 1). Most of the studies only make a first attempt to integrate a number of important sustainable development indicators and only a few have considered the implications for CCS (Turkenburg, 1997). To date studies have focused on short-term side-impacts of climate change mitigation policies (e.g. local air and water quality impacts) but have also suggested a number of additional indicators to reflect development (e.g. employment generation) and social impacts (e.g. income distribution). CCS also poses issues of long term liability arising from possible unintended release or contamination which may have inter-generational and, in some cases, international consequences[24] - further studies will be needed to develop suitable answers about CCS. In particular, long-term liability has to be demonstrated to be compatible with sustainable development.

There are various perspectives on climate policy - one is cost-effectiveness, another is environmental sustainability, and another is equity (Munasinghe and Swart, 2005). Most policies designed to achieve mitigation of climate change also have other important rationales e.g. related to objectives of development, sustainability and equity. “Conventional” climate policy analyses have tended to be driven (directly or indirectly) by the question: what is the cost-effective means of mitigating climate change for the global economy? Typically this starts from a baseline projection of greenhouse gas emissions and reflects a specific set of socio-economic projections. Equity considerations are added to the process, to broaden the discussion from global welfare as a single subject to include the effects of climate change and mitigation policies on existing inequalities, amongst and within nations. Beyond providing for basic survival, this strives for a standard of living that provides security and dignity for all.

Ancillary effects of mitigation policies may include reductions in local and regional air pollution, as well as indirect effects on transportation, agriculture, land use practices, biodiversity preservation, employment, fuel security, etc. (Krupnick *et al.*, 2000). The concept of “co-benefits” can be used to capture dimensions of the response to mitigation policies from the equity and sustainability perspectives in a way that could modify the projections produced by those working from the cost-effectiveness perspective. As yet, little analysis has been reported of the option of CCS in these respects.

Will CO_2 capture and storage favour the creation of job opportunities for particular countries? Will it favour technological and financial elitism or will it enhance equity by reducing the cost of energy? In terms of sustainable development, does the maintenance of the current market structures aid those countries that traditionally market fossil fuels, relative to those that import them? Is this something which mitigation policies should be developed to assist? There are no simple answers to these questions but policy makers may want to consider them in developing policy. However no analysis of CCS in these respects is yet available. Furthermore, the mitigation options available will

[24] Some legislation is already in place which will influence this – for example both the London Convention (Article X) and its 1996 Protocol (Article 15) contain provisions stating that liability is in accordance with the principles of international law regarding a state’s responsibility for damage caused to the environment of other states or to any other area of the environment. Similarly, regional agreements such as the OSPAR Convention incorporate the principle of “polluter pays” (Article 2(b)).

vary from country to country - in each case, policy-makers have to balance such ancillary benefits with the direct benefits of the various options in order to select the most appropriate strategy.

1.7.2 Technology transfer

Article 4.5 of the UNFCCC requires that all Annex I countries should take "All practicable steps to promote, facilitate and finance, as appropriate, the transfer of, or access to, environmentally sound technologies and know-how to other parties, particularly developing countries, to enable them to implement provisions of the convention.". This applies to CCS as much as it does to any other mitigation option. This was precisely stated in the declaration issued at COP 7 (UNFCCC, 2001). Paragraph 8, item (d) states:

"Cooperating in the development, diffusion and transfer (…) and/or technologies relating to fossil fuels that capture and store GHGs, and encouraging their wider use, and facilitating the participation of the least developed countries and other Parties not included in Annex I in this effort"

In achieving these objectives of the Convention, several key elements will have to be considered (IPCC, 2001a). These are discussed in the IPCC Special Report on Technology Transfer (IPCC, 2000c), which looked into all aspects of the processes affecting development, application and diffusion of technology. This looks at technology transfer for purposes of adapting to climate change as well as for mitigation. It looks at processes within countries and between countries. It covers hardware, knowledge and practices. Particularly important are assessment of technology needs, provision of technology information, capacity building, creation of an enabling environment, and innovative financing to facilitate technology transfer.

Although no academic examination of CCS in these respects has yet been undertaken, some remarks can be made in general about this mitigation option in this respect.

1.7.2.1 Potential barriers

Technology transfer faces several barriers including intellectual property rights, access to capital, etc. As with any new technology, CCS opens opportunities for proprietary rights. As it will rely on development and/or integration of technologies, some of which are not yet used for such purposes, there is considerable scope for learning by doing. Several developing countries are already taking active interest in this option, where they have national resources that would allow them to make use of this technique - for example, Deshun *et al.* (1998) have been looking at the related technique of CO_2-EOR. Some of the key technologies will be developed by particular companies (as is occurring with wind power and solar photovoltaics) but will the intellectual property about CCS be accumulated in the hands of a few? CCS will involve both existing and future technologies, some of which will be proprietary. Will the owners of these rights to be willing to exploit their developments by licensing others to use them? At present it appears to be too early to answer these questions.

Given that the essential parts of CCS systems are based on established technology, it can be expected that it will be accessible to anyone who can afford it and wants to buy it. Several companies currently offer competing methods of capturing CO_2; pipelines for CO_2 and ships are constructed today by companies specializing in this type of equipment; drilling of injection wells is standard practice in the oil and gas industry, and is carried out by many companies around the world. More specialist skills may be required to survey geological reservoirs; indeed monitoring of CO_2 underground is a very new application of seismic analysis. However, it is anticipated that,

within a short space of time, these will become as widely available as other techniques derived from the international oil and gas industry. Making these technologies available to developing countries will pose similar challenges as have been encountered with other modern technological developments. This shows the relevance of the UNFCCC declaration on technology transfer quoted above to ensure that developing countries have access to the option to capture and store CO_2.

1.7.2.2 Potential users

CO_2 emissions are rising rapidly in some developing countries; if these countries wish to reduce the rate of increase of emissions, they will want to have access to a range of mitigation options, one of which could be CCS. Initially it seems likely that CCS would be exploited by countries with relevant experience, such as oil and gas production[25], but this may not be the case in other natural resource sectors. Will the opportunity for transfer of CCS technology be less than with other mitigation options where technologies are spread out in the hands of many companies? Or will the knowledge and experience already available in the energy sector in certain developing countries provide an opportunity for them to exploit CCS technologies? Will CO_2 capture and storage technologies attract more interest from certain developing countries if applied to biomass sources[26]? If there is a year-round supply of CO_2 from the biomass processing plant and good storage reservoirs within reasonable distance, this could be an important opportunity for technology transfer. As yet there are no answers to these questions.

1.8 Contents of this report

This report provides an assessment of capture and storage of CO_2 as an option for mitigation of climate change. The report does not cover the use of natural sinks to sequester carbon as that is covered in the Land Use, Land Use Change and Forestry report (IPCC, 2000b) and in IPCC's Third Assessment Report (IPCC, 2001a).

There are many technical approaches which could be used for capturing CO_2 – these are examined in Chapter 3, with the exception of biological processes for fixation of CO_2 from flue gases which are not covered in this report. The main natural reservoirs which could, in principle, hold CO_2 are geological formations and the deep ocean - these are discussed in Chapters 5 and 6 respectively. Other options for storage and re-use of CO_2 are examined in Chapter 7.

Chapter 2 considers the geographical correspondence of CO_2 sources and potential storage reservoirs, which will determine the cost-effectiveness of moving CO_2 from the place where it is captured to the storage site. A separate chapter, Chapter 4, covers the methods of transporting CO_2 from capture to storage site.

The overall cost of this technology and the consequences of including it in energy systems models are described in Chapter 8. Some of the other requirements, which have been outlined above, such as legality, applicable standards, regulation and public acceptance are discussed in detail at the appropriate point in several of the chapters. Governments might also wish to know how this method of emission reduction would be taken into account in national inventories of greenhouse gas emissions, which is discussed in Chapter 9. Government and industry alike will be interested in the accessibility of the technology, in methods of financing the plant and whether assistance will be

[25] In 1999, there were 20 developing countries each producing more than 1% of global oil production, 14 developing countries each producing more than 1% of global gas production, and 7 developing countries producing more than 1% of global coal production (BP, 2003).

[26] For further discussion of using CCS with biomass, see Chapter 2.

available from industry, government or supra-national bodies. At present it is too early in the exploitation of this technology to make confident predictions about these matters. Two Appendices provide information on the properties of CO_2 and carbon-containing fuels, and a glossary of terms. Gaps and areas for further work are discussed in the chapters and in the Technical Summary to this report.

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Tables

Table 1.1. Sources of CO_2 emissions from fossil fuel combustion (2001).

	Emissions	
	(Million tonnes CO_2/y)	**(Million tonnes C/y)**
Public Electricity and Heat Production	8,236	2,250
Autoproducers	963	263
Other Energy Industries	1,228	336
Manufacturing & Construction	4,294	1,173
Transport	5,656	1,545
of which: Road	4,208	1,150
Other Sectors	3,307	903
of which: Residential	1,902	520
TOTAL	23,684	6,470

Source: IEA, 2003.

Figures

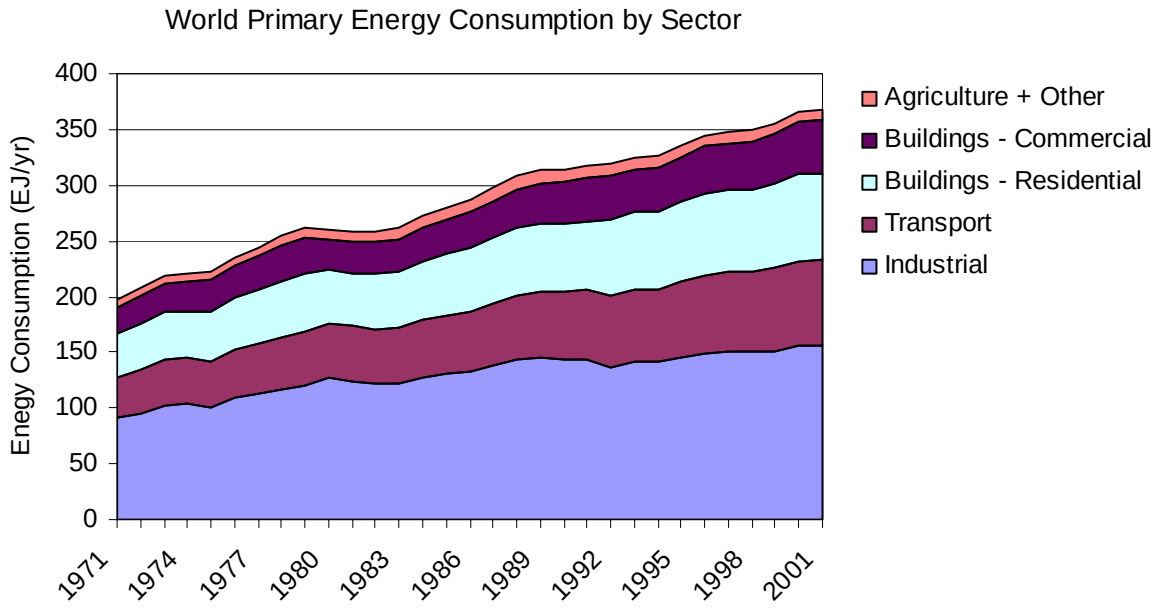

Figure 1.1. World primary energy use by sector from 1971 to 2001 (IEA, 2003). These statistics exclude traditional biomass; the energy industries (e.g. oil refining) are included in the Industrial sector.

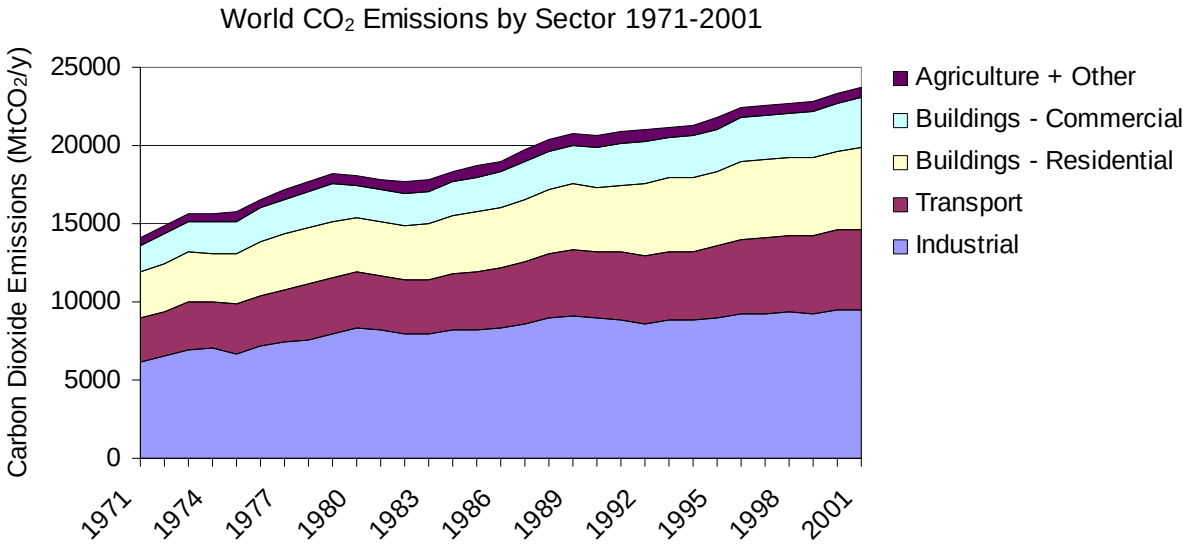

Figure 1.2. World CO_2 emissions from fossil fuel use by sector, 1971 to 2001 (IEA, 2003). Energy industries (e.g. oil refining) are included in the Industrial sector.

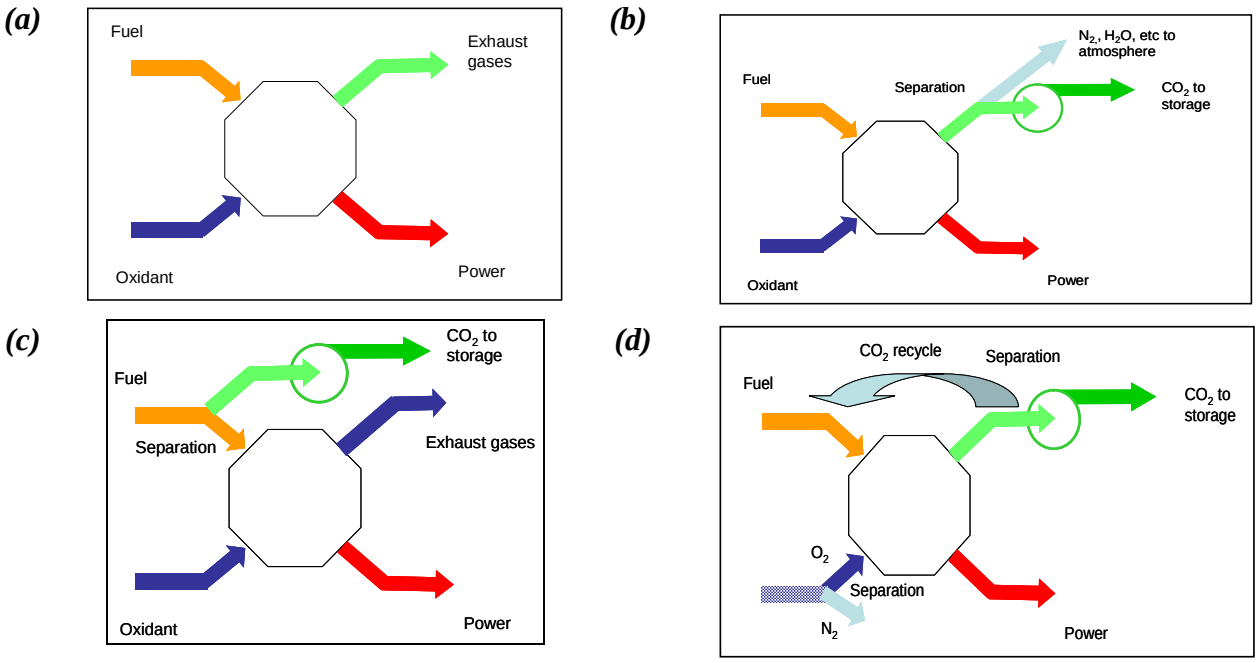

Figure 1.3. (a) Schematic diagram of fossil fuel based power generation; (b) Schematic diagram of Post-combustion capture; (c) Schematic diagram of Pre-combustion capture; (d) Schematic diagram of Oxyfuel combustion.

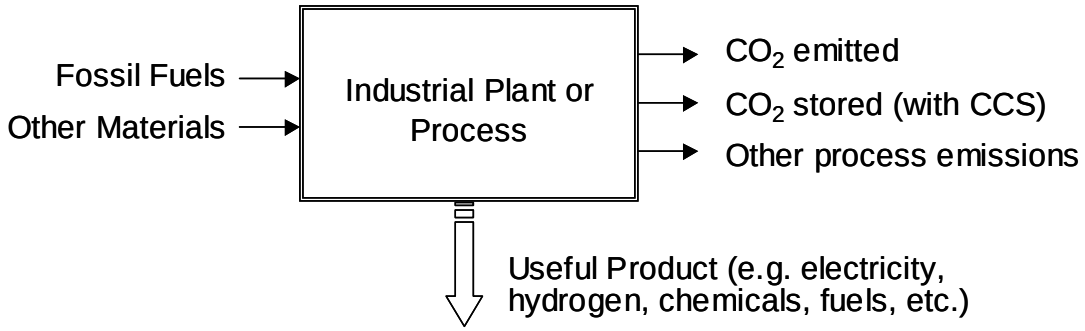

Figure 1.4. System boundary for a plant or process emitting CO_2 (such as a power plant, a hydrogen production plant or other industrial process). The resource and environmental impacts of a CCS system are measured by the changes in total system input and output quantities needed to produce a unit of product.

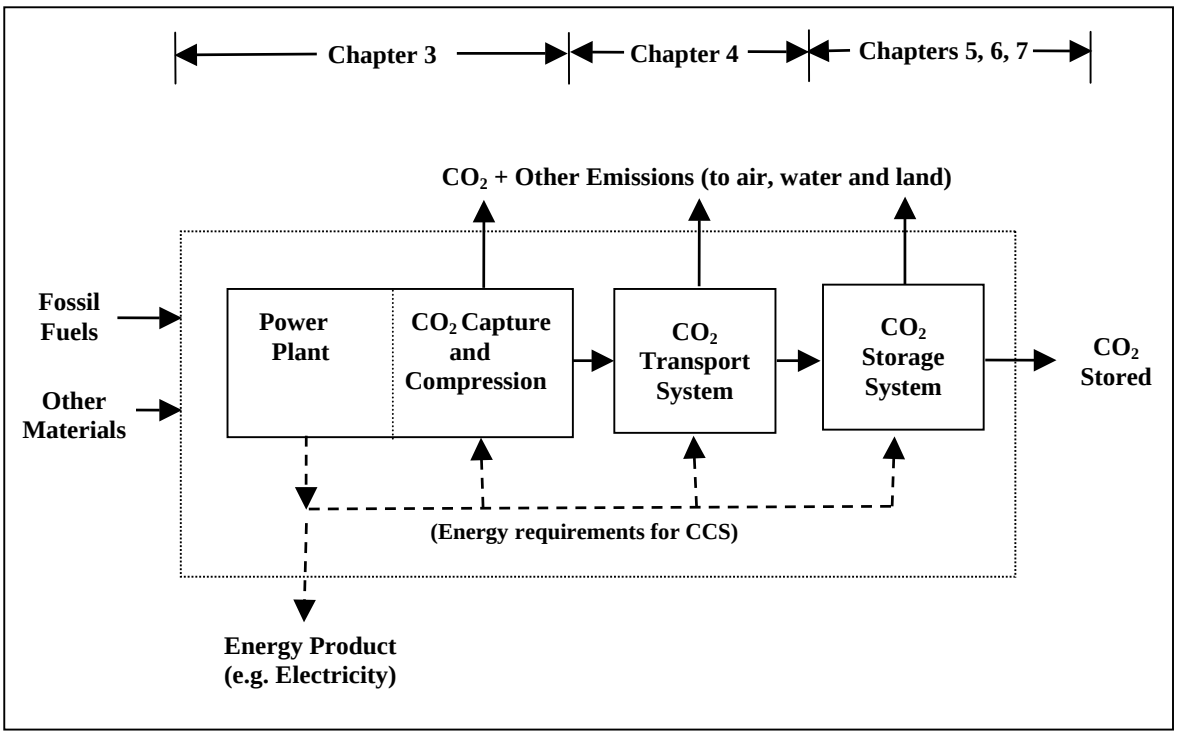

Figure 1.5. System components inside the boundary of Figure 1.4 for the case of a power plant with CO_2 capture and storage. Solid arrows denote mass flows while dashed lines denote energy flows. The magnitude of each flow depends upon the type and design of each sub-system, so only some of the flows will be present or significant in any particular case. To compare a plant with CCS with another system having similar product, e.g. a renewables-based power plant, a broader system boundary may have to be used.

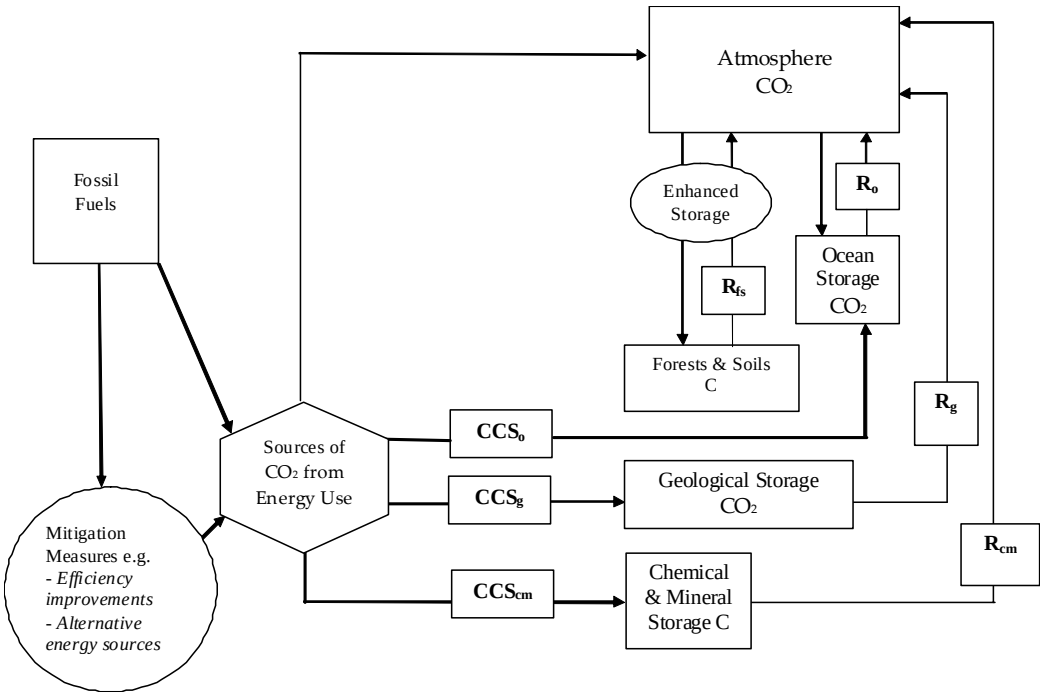

Figure 1.6. Schematic diagram of stocks and flows of CO_2 with net flows of captured CO_2 to each reservoir indicated by the label CCS (these flows exclude residual emissions associated with the process of capture and storage). The R-values indicate the rates of leakage from each of the storage reservoirs. The stock in the atmosphere depends upon the difference between the rates at which CO_2 reaches the atmosphere and at which it is removed. Flows to the atmosphere may be slowed by a combination of mitigation options, such as improving energy efficiency or use of alternatives to fossil fuels, by enhancing biological storage or by utilizing CCS in geological formations, in the oceans or in chemicals or minerals.

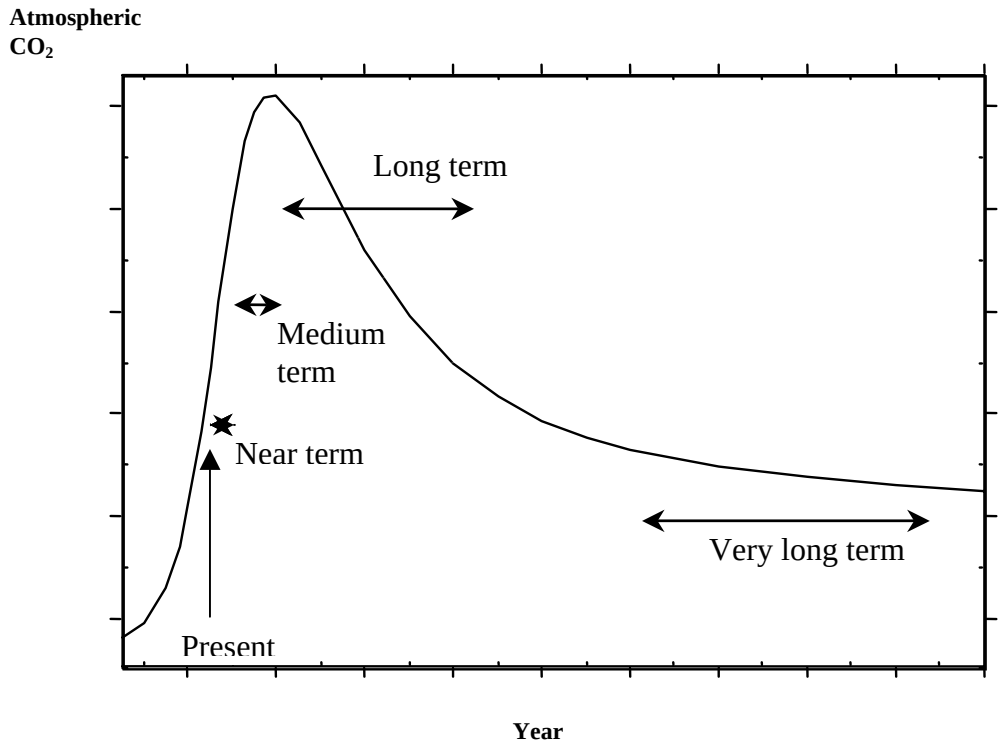

Figure 1.7. The response of atmospheric CO_2 concentrations due to emissions to the atmosphere. Typical values for "near-term", "medium-term", "long-term" and" very long-term" are years, decades, centuries, millennia, respectively. In this example, cumulative emissions are constrained to a maximum value and concentrations stabilise at 550 ppmv (adapted from Kheshgi, 2003). This figure is indicative and should not be read as prescribing specific values for any of these periods. If the goal were to constrain concentrations in the atmosphere to lower levels, such as 450 ppmv, greater reductions in emission rates would be required.

2. Sources of CO_2

Coordinating Lead Author

JOHN GALE (UNITED KINGDOM)

Lead Authors

John Bradshaw (Australia), Zhenlin Chen (China), Amit Garg (India), Dario Gomez (Argentina), Hans-Holger Rogner (Germany), Dale Simbeck (United States), Robert Williams (United States)

Contributing Authors

Ferenc Toth (Austria), Detlef van Vuuren (Netherlands)

Review Editors

Ismail El Gizouli (Sudan), Jürgen Friedrich Hake (Germany)

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Executive Summary

Assessing CO_2 capture and storage calls for a comprehensive delineation of CO_2 sources. The attractiveness of a particular CO_2 source for capture depends on its volume, concentration and partial pressure, integrated system aspects, and its proximity to a suitable reservoir. Emissions of CO_2 arise from a number of sources, predominately from fossil fuel combustion in the power generation, industrial, residential and transport sectors. In the power generation and industrial sectors, many sources have large emission volumes that make them amenable to the addition of CO_2 capture technology. Large numbers of rather small point and, in the case of transportation, mobile sources characterize the other sectors, which currently makes them less amenable for capture. Technological changes in the production and nature of transportation fuels, however, may eventually allow the capture of CO_2 from energy use in this sector.

Over 7,500 large CO_2 emission sources (above 0.1 $MtCO_2$/yr) have been identified. These sources are distributed geographically around the world but four clusters of emissions can be observed. Emission clusters arise in the North America (mid-west and eastern freeboard of USA), Europe (North West), South East Asia (eastern coast) and South Asia (Indian sub-continent). In the future (up to 2050) it is projected that the number of emission sources from the power and industry sectors is likely to increase. According to these projections, the increase in emission sources is expected to predominantly occur in Southern and South Eastern Asia, while the number of emission sources suitable for capture and storage in regions like Europe may decrease slightly.

Comparing the geographical distribution of the emission sources with geological storage opportunities it can be seen that globally there is a good relationship between the sources and opportunities. A substantial proportion of the emission sources lie either on top of or within a distance of 300 km from a site that has potential for geological storage. Detailed studies are, however needed to confirm the suitability of such sites for CO_2 storage. In the case of ocean storage, based on related research it is expected that only a small proportion of large emission sources will be close to potential ocean storage sites.

The majority of the emissions sources have concentrations of CO_2 of typically less than 15%. However, a small proportion (less than 2%) has concentrations greater than 95%, which makes them more favourable for CO_2 capture. The high content sources offer the prospect for lower capture costs, compared to low content sources, because only dehydration and compression is required. The future proportion of high and low content CO_2 sources is largely a function of the rate of introduction of hydrogen, biofuels, and gasification or liquefaction of fossil fuels as well as how future plant sizes are going to unfold.

Technological changes, such as the centralized production of liquid or gaseous energy carriers (e.g., methanol, ethanol or hydrogen) from fossil sources or centralized production of such energy carriers or electricity from biomass may allow for CO_2 capture and storage. Under these conditions, power generation and industrial emission sources would largely remain unaffected but small transport and distributed energy supply system CO_2 emissions would be replaced by additional point sources that would be amenable to capture. The CO_2 could then be stored either in geological formations or in the oceans. Based on the scarcity of data it is not possible to project the likely numbers of such additional point sources, or their geographical distribution with confidence (estimates range from 0 to 1,400 $GtCO_2$ (0 - 380 GtC) for 2050).

According to six illustrative SRES scenarios, global CO_2 emissions may range between 29.3 and 44.2 $GtCO_2$ (8 - 12 GtC) for 2020 and 22.5 and 83.7 $GtCO_2$ (6 - 23 GtC) for 2050. The technical potential of CO_2 capture associated with these emission ranges have been recently estimated at 2.6-

4.9 $GtCO_2$ by 2020 (0.7.- 1.3 GtC) and 4.9-37.5 $GtCO_2$ by 2050 (1.3 - 10 GtC). These emission and capture ranges reflect the inherent uncertainties of scenario and modelling analyses. But certain trends are uniform across the six illustrative SRES scenarios: the general increase of future CO_2 emissions in the developing countries relative to the industrialized countries.

2.1 Sources of CO_2

This chapter aims to consider the emission sources of CO_2 and their suitability for capture and subsequent storage both currently and in the future. In, addition it considers alternative energy carriers to fossil fuels and how the future development of this technology might affect the global emission sources of CO_2 and the suitability of capturing these emissions.

Chapter 1 has identified that the power and industry sectors combined dominate current global CO_2 emissions contributing about 60% of the total CO_2 emissions (see Section 1.2.2). Future projections indicate that the share of these sectoral emissions will decline to around 50% of global CO_2 emissions by 2050 (IEA, 2002). The CO_2 emissions in these sectors are typically generated from boilers and furnaces burning fossil fuels and are typically emitted from large exhaust stacks. These stacks can be termed as large stationary sources, to distinguish them from mobile sources such as those generated in the transportation sector and from smaller stationary sources such as small heating boilers used in the residential sector. The large stationary sources represent potential opportunities for the addition of CO_2 capture plant. The volumes produced from these sources are usually large and the plants can be equipped with a capture plant to produce a source of high purity CO_2 for subsequent storage. Of course, not all power generation and industrial sites produce their emissions from a single point source. At large industrial complexes like refineries there will be multiple exhaust stacks, which require an additional technical challenge in terms of integrating an exhaust gas gathering system onto an already congested complex that will undoubtedly add to capture costs (Simmonds et al, 2003).

In the power sector, coal is currently the dominant fuel accounting for 38% of electricity generated in 2000 with hydro power 17.5%, natural gas, 17.3%, nuclear 16.8%, oil 9%, non hydro renewables 1.6%. By 2020, coal is projected to remain the dominant fuel for power generation (~36%), whilst natural gas generation will become the second largest source surpassing hydro. The use of biomass as a fuel in the power sector is currently limited. Fuel choice in the industrial sector is to a large extent sector specific. For example, in the iron and steel sector the use of blast furnaces dominates primary steel production, which uses primarily coal and coke (IEA GHG, 2000b; IPCC, 2001). In the refining and chemical sectors, oil and gas are the primary fuels. For industries like cement manufacture all fossil fuels are used, with coal dominating in areas like USA, China and India (IEA GHG, 1999), and oil and gas in countries like Mexico (Sheinbaum and Ozawa, 1998). However in European cement manufacture, there is now a trend to use non-fossil fuels, principally wastes like tyres, sewage sludge and chemical waste mixtures (IEA GHG, 1999). In global terms biomass is not typically a significant fuel source in the large manufacturing industries. However, it is acknowledged in certain regions of the world, like Scandinavia and Brazil, biomass use can be significant (Möllersten et al, 2003).

To reduce the CO_2 emissions from the power and industry sectors, through the use of CO_2 capture and storage, it is important to understand where these emissions arise and what their geographical relationship is with respect to potential storage opportunities (Gale, 2002). If there is a good geographical relationship between the large stationary emission sources and potential geological storage sites then it is possible that a significant proportion of the emissions from these sources can be reduced using CO_2 capture and storage. If, however, they are geographically not well matched,

then there will be implications on the length and size of the transmission infrastructure that is required which could impact significantly on the cost of CO_2 capture and storage and the potential to achieve deep reductions in global CO_2 emissions. It may be the case that there are regions of the world that have greater potential for the application of CO_2 capture and storage than others, based on their source/storage opportunity relationship. Understanding the regional differences will be an important factor in assessing how much of an impact CO_2 capture and storage can have on global emissions reduction and which of the portfolio of mitigation options is most important from a regional context.

Other sectors of the economy, such as residential and transport sectors contribute around 30% of global CO_2 emissions and also produce a large number of point source emissions. However the emission volumes from the individual sources in these sectors tend to be small in comparison to those from the power and industry sectors and are much more widely distributed, or even mobile rather than stationary. It is currently not considered to be technically possible to capture emissions from these other small stationary sources, because there are still substantial technical and economic issues that need to be resolved (IPCC, 2001). However, in the future, the use of low-carbon energy carriers, such as electricity or hydrogen produced from fossil fuels, offers the prospect for CO_2 emissions to be captured from the residential and transport sectors as well. Such fuels would most probably be produced in large centralized plants and would be accompanied by capture and storage of the CO_2 co-product. The distributed fuels could then be used for distributed generation in either heaters or fuels cells and in vehicles in the transport sector. In this scenario, power generation and industrial sources would be unaffected but additional points sources would be generated that would also require being stored. Therefore, in the medium to long term, the development and commercial deployment of such technology combined with an accelerated shift to low or zero carbon fuels in the transportation sector could potentially lead to a significant change in the geographical pattern of CO_2 emissions compared to that currently observed.

2.2 Characterization of CO_2 emission sources

This section presents information on the characteristics of the CO_2 emission sources, it is considered necessary to review the different CO_2 contents and volumes of CO_2 produced from these sources as these factors can influence the technical suitability of these emissions for storage and the costs of capture and storage.

2.2.1 Present

2.2.1.1 Source types

The emission sources considered in this chapter include all large stationary sources (>0.1 $MtCO_2$/yr) arising from fossil fuel and biomass use. These sources are present in three main areas: fuel combustion activities, industrial processes and natural gas processing. By far the largest CO_2 emissions result from the oxidation of carbon when fossil fuels are burned. This type of source arises from fossil fuel combustion in power plants, oil refineries and large industrial facilities. Large stationary sources for this report are taken as those emitting over 0.1 $MtCO_2$/yr. This threshold was selected because the sources emitting less than 0.1 $MtCO_2$/yr cumulative emit less than 1% of the emissions from all the stationary sources under consideration (see Figure 2.1). However, this threshold does not exclude smaller CO_2 sources from capturing their emissions although this becomes more technically challenging, in the case of distributed sources, and costly.

Carbon dioxide not related to combustion is emitted from a variety of industrial production processes which chemically, physically or biologically transform materials. Such processes include:

- The use of fuels as feed stocks in petrochemical processes (Chauvel and Lefebvre, 1989; Christensen and Primdahl, 1994),
- The use of carbon as a reducing agent in the commercial production of metals from ores (IEA GHG, 2000; IPCC, 2001),
- The thermal decomposition (calcination) of limestone and dolomite in cement or lime production (IEA GHG, 1999, IPCC 2001),
- The fermentation of biomass (e.g. to convert sugar to alcohol).

In some instances these industrial process emissions are produced in combination with fuel combustion emissions, a typical example is aluminium production (IEA GHG, 2000).

A third type of source occurs in natural gas processing installations. CO_2 is a common impurity in natural gas which must be removed to improve the heating value of the gas or to meet pipeline specifications (Maddox and Morgan, 1998).

2.2.1.2 CO_2 content

The properties of those streams that can be input to a CO_2 capture process are discussed in this section. For CO_2 capture not only the concentration of the gas stream to be treated is important, but also its CO_2 partial pressure. The latter which, for practical purposes, can be defined as the product of the total pressure of the gas stream times the CO_2 mole fraction, is a key variable in the selection of the separation method (this is discussed further in Chapter 3). As a rule of thumb, it can be said that the lower the CO_2 partial pressure of a gas stream, the more stringent conditions are presented to the separation process.

Typical CO_2 concentrations and their corresponding partial pressures for large stationary combustion sources are shown in Table 2.1, which also includes the newer Integrated Gasification Combined Cycle technology (IGCC). Typically the majority of emission sources from the power sector and from industrial processes have low CO_2 partial pressures, hence the focus of the discussion in this section. Where high partial pressure emission sources are generated, for example in ammonia or hydrogen production these sources require only dehydration and some compression and hence lower capture costs.

The properties of CO_2 streams originating from cement and metal production that combine both chemical transformations and combustion are also summarized in this Table. Flue gases found in power plants, furnaces in industries, blast furnaces and cement kilns are typically generated at atmospheric pressure and temperatures ranging between 100°C to 200°C depending on the heat recovery conditions.

Table 2.1. Properties of candidate gas streams that can be input to a capture process.

Carbon dioxide content in flue gases varies depending on the type of fuel used and the excess air level used for optimal combustion conditions. Flue gas volumes depend also on these two variables. Natural gas fired power generation plants are typically combined cycle gas turbines which generate flue gases with low CO_2 concentrations, typically 3-4% by volume (IEA GHG, 2002a). Coal, for power generation is primarily burnt in pulverized fuel boilers producing an atmospheric pressure flue gas stream with a CO_2 content of up to 14% by volume (IEA GHG, 2002a). The newer and potentially more efficient IGCC technology has been developed for generating electricity from coal, heavy fuel oil and process carbonaceous residues. In this process the feedstock is first gasified to

generate a synthesis gas (often referred to as "syngas"), which after exhaustive gas cleaning is burnt in a gas turbine (Campbell et al., 2000). Current IGCC plants where the synthesis gas is directly combusted in the turbine, like conventional thermal power plants, produce a flue gas with low CO_2 concentration (up to 14% by volume). Currently only fifteen coal and oil fired IGCC plants ranging in size from 40 to 550 MW have been started up in 1980s and 1990s in Europe and the USA (Giuffrida et al., 2003). It is noted that there are conceptual designs in which the CO_2 can be removed before the synthesis gas is combusted which produces a high concentration, high pressure CO_2 exhaust gas stream that could be more suitable for storage (See Chapter 3 for more details). However, it is noted that no such plants have been built or are under construction.

Fossil fuel consumption in boilers, furnaces and in process operations in the manufacturing industry also typically produces flue gases with low CO_2 contents comparable to those in the power sector. The CO_2 concentration in the flue gas from cement kilns depends on the production process and type of cement produced and is usually higher than in power generation processes (IEA GHG, 1999). Existing cement kilns in developing countries such as China and India are often relatively small. However, the quantity of CO_2 produced by a new large cement kiln can be similar to that of a power station boiler. Integrated steel mills globally account for over 80% of CO_2 emissions from steel production (IEA GHG, 2000b). About 70% of the carbon input to an integrated steel mill is present in the blast furnace gas, which is used as fuel gas within the steel mill. CO_2 could be captured before or after combustion of this gas. The CO_2 concentration after combustion in air would be about 27% by volume, significantly higher than in the flue gas from power stations. Other process streams within a steel mill may also be suitable candidates for CO_2 capture, before or after combustion, for example the off-gas from an oxygen-steel furnace contains typically 16% CO_2 and 70% carbon monoxide.

The off-gases produced during the fermentation of sugars to ethanol consist of almost pure CO_2 with a few impurities (and a familiar aroma). This gas stream is generated at a rate of 0.76 kg CO_2/litre and is typically available at atmospheric pressure (0.1 MPa) Kheshgi and Prince (2005).

CO_2 also occurs as a non-desired product that must be removed in some petrochemical process, particularly those using synthesis gas as an intermediate or as an impurity in natural gas. The properties of the raw gas streams from which CO_2 is customarily removed in some of these industries are shown in Table 2.2. It can be seen from Table 2.1 that the CO_2 partial pressures of flue gases are at least one order of magnitude less than the CO_2 partial pressures of the streams arising from the processes listed in Table 2.2. This implies that CO_2 recovery from fuel combustion streams will be comparatively much more difficult.

Table 2.2. Typical properties of gas streams that are already input to a capture process.

2.2.1.3 Scale of emissions

A specific detailed dataset for CO_2 stationary sources in 2000, giving their geographical distribution by process type and country has been developed (IEA GHG, 2002a). The stationary sources of CO_2 of this database comprise power plants, oil refineries, gas processing plants, cement plants, iron and steel plants and those industrial facilities where fossil fuels are used as feedstock namely ammonia, ethylene, ethylene oxide and hydrogen. This global inventory contains over 14 thousand emission sources with individual CO_2 emissions ranging from 2.5 tCO_2/yr to 55.2 $MtCO_2$/yr. The information for each single source includes location (city, country and region), annual CO_2 emissions and CO_2 emission concentrations. The coordinates (latitude/longitude) of 74% of the sources are also provided. The total emissions from these 14 thousand sources amount to over 13 $GtCO_2$/yr. Almost 7,900 stationary sources whose individual emission are greater than or equal to

0.1 $MtCO_2$ per year have been identified globally. These emissions comprise over 90% of total large point source CO_2 emissions in 2000 (see Figure 2.1). Some 6,000 emission sources with emissions below 0.1$MtCO_2$/yr were also identified but since these represent only a small fraction of the total emissions volume they were excluded from further discussion in this chapter. There are also a number of regional and country specific CO_2 emission estimates for large sources covering China, Japan, India, North West Europe and Australia (Hibino, 2003; Garg et al., 2002; Christensen et al., 2001, Bradshaw et al., 2002) that can be drawn upon. Table 2.3 summarizes the information concerning large stationary sources according to the type of emission generating process. For the petrochemical and gas processing industries, the CO_2 concentration listed in this Table refers to the conditions of the stream leaving the capture process. The largest amount of CO_2 emitted from large stationary sources originates from fossil fuel combustion for power generation with an average annual emission of 3.9 $MtCO_2$ per source. Substantial amounts of CO_2 arise in the oil and gas processing industries while cement production is the largest emitter from the industrial sector.

In the USA, 12 ethanol plants with a total productive capacity of 5.3 billion litres/yr each produce CO_2 at rates in excess of 0.1 $MtCO_2$/yr, (Kheshgi and Prince, 2005): In Brazil, where ethanol production totalled over 14 billion litres per year during 2003-2004 the average distillery productive capacity is 180 million litres/y. The corresponding average fermentation CO_2 production rate is 0.14 $MtCO_2$/yr, with the largest distillery producing nearly 10 times the average.

Table 2.3. Profile of worldwide large CO_2 stationary sources emitting more than 0.1 Mt CO_2 per year (Source: IEA GHG, 2002a).

The top 25% of all large stationary CO_2 emission sources (emitting individually more than 1 Mt CO_2 per year) considered in Table 2.3, contribute over 85% of the cumulative emissions from these types of sources. On the opposite side the lowest 41%, within the range 0.1 to 0.5 $MtCO_2$ per source contributes less than 10% (Figure 2.1). There are 330 sources with individual emissions above 10 Mt CO_2 per year, with 78% of their cumulative emissions contributed by power plants, 20% by gas processing and the remaining by iron and steel plants (IEA GHG, 2000b). High concentration/partial pressure sources (e.g. from ammonia/hydrogen production and gas processing operations) contribute a relatively low share (<2%) of the emissions from large stationary sources (van Bergen et al, 2004). However, these high concentration sources can represent early prospects for the implementation of CO_2 capture and storage. The costs for capture are lower than for low concentration/ partial pressure sources. Then, if these sources can be linked to enhanced production schemes like CO_2-enhanced oil recovery which are close to their location (<50km), they can become low costs options for CO_2 capture and storage (van Bergen et al, 2004). Such sources emit annually 0.36 $GtCO_2$/yr (0.1 GtC/yr), which equates to 3% of the large point sources emissions larger than 0.1 $MtCO_2$/yr (IEA GHG, 2002b). The geographical relationship between these high concentration sources and prospective storage opportunities is discussed in Section 2.3.3. A small number of high CO_2 concentration source streams are already used in CO_2-EOR operations in the USA and Canada (Stevens and Gale, 2000).

Figure 2.1. Relationship between large stationary source emissions and number of emission sources (Source: IEA GHG 2002a).

2.2.2 Future

Future anthropogenic CO_2 emissions are the product of different driving forces such as demographic development, socio-economic development, and technological changes (see Chapter 1, Section1.2.4). Because their future evolution is inherently uncertain and the numerous combinations

of different rates of change that are reasonably possible, analysts resort to scenarios as a means to describe internally consistent alternative images of how the future might unfold. The IPCC developed a set of greenhouse gas emission scenarios out to the year 2100 (IPCC, 2000). The scenarios lead to a wide range of possible future worlds and CO_2 emissions (see Figure 2.2) consistent with the full uncertainty range of the underlying literature reported by Morita and Lee, 1998. The scenarios are important as they provide a backdrop for determining the baseline for emission reductions that may be achieved with new technologies including CO_2 capture and storage especially implemented for such purposes.

Figure 2.2. Range of annual global CO_2 emissions in the SRES scenarios ($GtCO_2$). Source: IPCC, 2000).

Technology change is one of the key drivers in long-term scenarios and plays a critical role in the SRES scenarios. Future rates of innovation and diffusion are integral parts of, and vary with, the story lines. Scenario-specific technology change may differ in terms of technology clusters (which type of technologies) or rate of diffusion. In the fossil intensive A1FI scenario, innovation concentrates on the fossil source to service chains, i.e., from exploration and resource extraction to fuel upgrading/cleaning, transportation, conversion and end-use while innovation in the environmentally oriented B1 scenario focuses on renewable and hydrogen technologies.

The way in which technology change entered the SRES scenarios was model specific. Some models applied autonomous performance improvements on fuel utilization while others included specific technologies with detailed performance parameters. Even models with a high technology resolution reflected new technologies or innovation in a rather generic manner. For example, advanced coal technology could be either an integrated coal gasification combined cycle (IGCC) plant, a pressurized fluidized bed combustion facility or any other yet to be identified technology. The main characteristics of advanced coal technology are attractive investment costs, high thermal efficiency, potential multi-production integration and low pollution emissions – features that are prerequisites for any coal technology carrying the “advanced” label.

In general, technology diversity remained a feature in all scenarios, despite the fact that one cluster may dominate more in one scenario and another more in other scenarios. The trend towards cleaner and more convenient technologies, especially at the level of end-use (including transportation), is common to all scenarios. As well, transportation fuels shift more or less towards supply schemes suitable for pre-combustion decarbonization. Centralized non-fossil technologies penetrate the power sector at varying degrees, while decentralized and home based renewable and hydrogen production infrastructure expand in all, but mostly in the environmentally conscious and technology intensive scenarios.

Despite the trend to cleaner fuels, CO_2 emissions are projected to rise at different rates at least until 2050, thereafter emission patterns diverge. Scenario specific rates of technology change (performance improvements) and technology diffusion lead to different technology mixes, fuel uses and unit sizes. As regards fossil fuel use for power generation and industrial energy supply, in the absence of restrictions on CO_2 emissions the number of large stationary emission sources generally increases and a fundamental change in the characteristics of these emission sources is unlikely to occur before 2050. As well, the ratio of low concentration to high concentration emission sources remains relatively stable, with low concentration sources dominating the emission profile.

After 2050, in some scenarios low or zero-carbon fuels such as ethanol, methanol or hydrogen begin to dominate the transport sector and make inroads in the industrial, residential and

commercial sectors. Centralized production of such fuels could potentially lead to a significant change in the number of high concentration emission sources and a change in the ratio of low to high purity emission sources; this is discussed in more detail in Section 2.4.3.

2.3 Geographical distribution of sources

This section discusses the geographical locations of the large point sources emissions considered in the preceding sections. It is necessary to understand how these large point sources emissions are geographically distributed across the world to assess their potential for subsequent storage.

2.3.1 Present

Knowledge of the geographical distribution of the sources of CO_2 emissions and the potential storage reservoirs assists the understanding the global cost of CO_2 mitigation, particularly those components associated with CO_2 transportation. Geographical information on emission sources can be retrieved from a number of data sets. The sectoral and regional distribution of energy related CO_2 emissions in 2000 is presented in Table 2.4. As discussed earlier in this report, over 60% of global CO_2 emissions come from the power and industry sectors. Geographically, these power and industry emissions are dominated by 4 regions having over 90% of the emissions. These regions are: Asia (30%), North America (24%), the transition Economies (13%), and OECD West[1] (12%). All other regions each have less than 6% of the global emissions from the power and industry sectors.

Table 2.4. Sectoral and regional distribution of energy-related CO_2 emissions in 2000 ($MtCO_2$) (Source: IEA, 2003).

The stationary CO_2 sources with known location worldwide, available from the database referred to in Section 2.2 (IEA GHG, 2002a), are plotted in Figure 2.3. North America is the region with the largest number of stationary sources (37%) followed by Asia (24%) and OECD Europe[2] (14%). Figure 2.3 indicates three large clusters of stationary sources, namely in the mid and eastern states of the US, in North western and central regions of Europe (Austria, Czech Republic, Germany, Hungary, Netherlands and UK) and in Asia, in eastern China and Japan with a further smaller cluster in the Indian subcontinent.

Figure 2.3. Global distribution of large stationary CO_2 sources (Source: IEA GHG, 2000a).

The distribution of stationary CO_2 emissions as a proportion of the total 2000 stationary emissions indicates that the regions that are the largest emitters of CO_2 from stationary sources are: Asia, 41% (5.6 $GtCO_2$/yr) > North America, 20% (2.69 $GtCO_2$/yr) > OECD Europe, 13% (1.75 $GtCO_2$/yr). All other regions emit less than 10% of the total CO_2 emission from stationary sources in 2000.

A comparison between the estimates of CO_2 emissions from the IEA and IEA GHG databases showed that the two sets produce similar estimates for the total of global emissions but results differ significantly for many countries. Such regional differences have also been noted for other CO_2 emission databases (Marland et al., 1999).

[1] Note: OECD West refers to the following countries: Austria, Belgium, Canada, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, Turkey, United Kingdom

[2] Note OECD Europe includes the OCED West countries listed previously plus Czech Republic, Hungary, Iceland, Norway, Poland, Slovak Republic, Switzerland and Turkey.

2.3.2 Future CO_2 emissions and technical capture potentials

The total CO_2 emissions from fossil fuel combustion of the SRES scenarios provide the upper limit for potential CO_2 capture for this assessment. In fact, the theoretical maximum is even higher because of the possibility of CO_2 capture from biomass. These emissions are also included in the tables of CO_2 emissions thus potentially available for capture. Obviously, the technically practical capture potential is much smaller than the theoretical maximum, and the economic potential[3] is even smaller. Needless to say, it is the economic potential that matters most. In this section, estimates of the technical potential are presented while Chapter 8 will address the economic potential.

Table 2.5 shows the CO_2 emissions by economic sector and major world regions for the year 2020 and 2050 for six scenarios[4]. Note the total CO_2 emissions in Table 2.5 are higher than reported in SRES because emissions from biomass are explicitly included here (as these are potentially available for capture) while they where considered "climate neutral" in the SRES presentations and thus not counted as emission releases to the atmosphere. Geographically, the distribution of emission sources is set to change substantially. Between 2000 and 2050 the bulk of emission sources would shift from the OECD countries to the developing regions, especially China, South Asia and Latin America. As to emissions by sector, power generation including other energy sector transformation, transport, and industry would remain the three main sources of CO_2 emission over the next 50 years. Globally, by 2050 the projected energy sector emissions fluctuate around the 40% mark (current share), the industry sector emissions decline while transport sector emissions (mobile sources) increase. Power generation, other energy sector transformation and industry, which typically represent the bulk of large point sources, account for ±50% of total emissions by 2050[5].

Table 2.5. Carbon dioxide emissions from sectors in major world regions in six IPCC SRES scenarios in 2020 and 2050 (IPCC, 2000).

These emissions form the theoretical maximum potential for CO_2 capture from fossil fuel use. Toth and Rogner (2005) derived a set of capture factors on the basis of technical or technological feasibility to add the required equipment to capture CO_2 before, during or after combustion of fossil fuels. Capture factors are defined as the maximum share of emissions estimated to be technically plausible to capture. A detailed assessment of the power plants currently in operation around the world and those planned to be built in the near future was conducted, together with a review of

[3] Economic potential is the amount of greenhouse gas emissions reductions from a specific option that would make sense economically, given prevailing circumstances (i.e. a price of CO_2 reductions and costs of other options)

[4] For the four marker scenarios and the technology-intensive A1T and the fossil-intensive A1FI illustrative scenarios. It is important to note that, it is not straightforward to compare the results of different models. First, the modelling methodologies imply different representations of energy technologies and their future evolutions. Second, the sectoral disaggregation and the energy/fuel details vary across the models. Third, there are differences in how countries of the world are grouped together into regions. Tables 2.5 and 2.6 are based on the work by Toth and Rogner (2005) attempts to create the best possible approximation to make the regional and sectoral model and scenario results comparable.

[5] As regards the share of emissions across sectors in 2020 (Table 2.5), there is an inherent divergence between scenarios with longer and shorter time horizons. Given the quasi perfect foresight of their underlying models, the SRES scenarios account for resource depletion over a period of a century and, due to the anticipated transition to higher fuel costs categories in the longer run, shift to non-fossil energy sources much earlier than say the IEA scenarios, especially for electricity supply. Consequently, the shares of fossil sourced power generation range between 43 and 58% by 2020 while the IEA projects a share of 71%. The corresponding sectoral shares in CO_2 emissions mirror the electricity generating mix: The IEA projects 43% for power generation (IEA, 2002) compared with 28 to 32% in the six illustrative SRES scenarios.

industrial boilers in selected regions. Capture factors were established on the basis of on installed capacity, fuel type, unit size, and other technical parameters. Outside the energy and industry sectors, there are only very limited prospects for practical CO_2 capture as sources in the residential sectors are small, dispersed, often mobile, and of low concentration resulting in lower capture factors.

In the assessment of CO_2 capture, perhaps the most important open question is what happens in the transport sector over the next few decades. If the above average increases in energy use for transportation projected by all models under all scenarios will involve traditional fossil-fuelled engine technologies then capture and storage of transport-related CO_2 - though theoretically possible – will remain technically meaningless (excess weight, on-board equipment, compression penalty, etc.). However, depending on the penetration rate of hydrogen-based transport technologies, it should be possible to retrofit CO_2 emitting hydrogen production facilities with CO_2 capture equipment. The transport sector provides a huge potential for indirect CO_2 capture but the feasibility depends on the eventual hydrogen production technologies.

CO_2 capture might also be technically feasible from biomass-fuelled power plants, biomass fermentation for alcohol production or biomass derived hydrogen production units. It is perfectly conceivable that these technologies might play a significant role by 2050 and produce negative emissions across the full technology chain.

The results of applying the capture factors developed by Toth and Rogner, 2005 to the CO_2 emissions of the SRES scenarios of Table 2.5 are presented in Table 2.6. Depending on the scenario, globally between 30 and 60% of the power generation emissions could be suitable for capture and storage by 2050 and 30 to 40% of industry emissions could also be captured in that time frame.

Table 2.6. CO_2 emissions available for capture and storage from sectors in major world region under six IPCC SRES scenarios in 2020 and 2050. Source: Toth and Rogner (2005).

The technical potentials for CO_2 capture presented here are only the first step in the full carbon dioxide capture and storage chain. The variations across scenarios reflect the uncertainties inherently associated with scenario and modelling analyses. The ranges of the technical capture potential relative to total CO_2 emissions are: 9 - 12% (or 2.6-4.9 $GtCO_2$) by 2020 and 21- 45 % (or 4.7 - 37.5 $GtCO_2$) by 2050.

2.4 Geographical relationship between sources and storage opportunities

The preceding sections of Chapter 2 have described the geographical distributions of CO_2 emission sources. This section gives an overview of the geographic distribution of potential storage sites that are in relative proximity to present day large point source emission sites.

2.4.1 Global storage opportunities

Global assessments of storage opportunities for CO_2 emissions, where large volumes of CO_2 storage are involved, have focused on the options of geological storage or ocean storage, where CO_2 is:

- injected and trapped within geological formations at subsurface depths greater than 800m where the CO_2 will be supercritical and in a dense liquid like form in a geological reservoir, or
- injected into deep ocean waters with the aim that it will disperse quickly or be deposited at great depths on the floor of the ocean with the aim that it would form lakes.

High level global assessments of both geological and ocean storage scenarios have estimated that they have large capacities (estimates range from 100s to 10,000's $GtCO_2$) to store CO_2. The storage capacity estimates in the literature in geological formations and in the oceans are discussed in detail in Chapters 5 and 6 respectively and are not discussed further in this chapter.

2.4.2 Consideration of spatial and temporal relationships

As discussed in Chapter 5, geological storage aims to replicate the natural occurrence of deep subsurface fluids, where they have been trapped for 10s to 100s of million of years. Due to the slow migration rates of subsurface fluids that can be observed in nature (often centimetres per year), and even including scenarios where CO_2 leakage to the surface might unexpectedly occur, CO_2 injected into the geological subsurface will essentially remain geographically nearby to the location that it is injected. In Chapter 6, it is shown that injection of CO_2 into the ocean water column does not remain in a static location, but will migrate at relatively rapid speed throughout the ocean as dissolved CO_2 within the prevailing circulation of ocean currents. Thus the dissolved CO_2 in the water column will not remain where it is injected in the immediate short term (years to 100s years). Deep ocean lakes of CO_2, in principle will be more static geographically, but will dissolve into the water column over years to centuries.

These spatial and temporal characteristics of migrating CO_2 in geological and ocean storage are important criteria when attempting to make maps of source and storage locations. In both storage scenarios, the possibility of future adjoining storage locations and the impact they might have upon each other will need to be considered.

2.4.3 Global geographical mapping of source/store locations

To appreciate the relevance of a map of the geographic distribution of sources and potential storage locations requires an awareness of the volumes of supply of CO_2 emissions and the storage capacity that might be available, and the types and level of technical uncertainties associated with the storage sites that will affect their viability as potential solutions. As indicated earlier in the chapter, there are some 7,500 large stationary sources with emissions over 0.1 $MtCO_2$/yr and that number is projected to rise by 2050. The mapping does not take into account the "capture factors" presented in Section 2.3.2.

2.4.3.1 Geological storage and source location matching

Chapter 5 includes detailed discussions of the geological characteristics of storage sites. Before discussing the global locations for geological storage opportunities, it is necessary to appreciate some basic fundamentals of geological storage. Geological provinces of the world can be categorized into a variety of rock types, but those principally of interest to geological storage are sedimentary basins that have undergone only minor tectonic deformation and are at least 1000m thick with adequate reservoir / seal pairs to allow for the injection and trapping of CO_2. The petroleum provinces of the world are a subset of the sedimentary basins described above, and are considered to be promising locations for geological storage of CO_2 (Bradshaw *et al,* 2002). Such basins have adequate reservoir / seal pairs, and suitable traps for hydrocarbons, be they either liquids or gases. The remaining geological provinces of the world can generally be categorized as igneous (rocks formed from crystallization of molten liquid) and metamorphic (pre-existing rocks formed by chemical and physical alteration due to heat, pressure and chemically active fluids) provinces. These rock types are commonly known as hard rock provinces, and they will not be favourable for CO_2 storage as they are generally not porous and permeable and thus will not readily

transmit fluids. More details on the suitability of sedimentary basins and characterization of specific sites are provided in Chapter 5.

Figure 2.4 shows the "prospectivity" (see Glossary) of various parts of the world for geological storage of CO_2. Prospectivity is a term commonly used in the exploration for any geological resource, in this case CO_2 storage space. Prospectivity is a qualitative assessment of the likelihood that a suitable storage location is present in a given area based on the available information. Being only a perception, it will change over time and with new information. The estimates of prospectivity are developed through examining data (if possible), examining existing knowledge, application of established conceptual models and ideally the generation of new conceptual models or applying an analogue from a neighbouring basin or some other geologically similar setting. The concept of prospectivity is often used when it is too complex or technically impossible to assign numerical estimates to the extent of a resource.

Figure 2.4 shows the geological provinces of the world categorized into provinces that are considered at a very simplistic level to comprise CO_2 storage potential that is either: 1) highly prospective, 2) prospective, or 3) non-prospective (Bradshaw and Dance, 2004). Areas of high prospectivity are considered to include those basins that are world-class petroleum basins, meaning that they are the basins of the world that are producing substantial volumes of hydrocarbons. It also includes areas that are expected to have substantial storage potential. Areas of prospective storage potential are basins that are minor petroleum basins but not world class, as well as other sedimentary basins that have not been highly deformed. Some of these basins will be highly prospective for CO_2 storage and others will have low prospectivity.

Determining the degree of suitability of any of these basins for CO_2 storage will be dependant on detailed work in each area. Areas that are non-prospective are highly deformed sedimentary basins and other geological provinces principally comprising metamorphic and igneous rocks. Some of these provinces might have some local niche opportunities for CO_2 storage, but at this stage they would not be regarded as representing a conventional form of CO_2 storage. As described by Bradshaw and Dance (2004), this map has significant caveats and assumptions associated with it due to the data source from which it was generated, but in general (not specific) can be used as a guide at the global scale to the location of areas that are likely to provide opportunities for geological storage CO_2. Due the generalized manner in which this map has been created, and the lack of specific or hard data from each of the basins assessed, the "prospectivity" levels assigned to each category have no meaningful correlative statistical or probabilistic connotation. To reach a numerical analysis of risk or certainty would require specific information on each and every basin assessed.

Figure 2.4. High level estimate of the CO_2 geological storage potential for sedimentary basins of the world (Bradshaw and Dance 2004).

Figure 2.5 shows the overlay of the sedimentary basins that are prospective for CO_2 storage potential with the current location of large stationary emission sources (IEA GHG, 2002a). The map can be simplistically interpreted to identify areas where large distances might be required to transport emissions from any given source to a geological storage location. It clearly shows areas with local geological storage potential and low number of emission sites (for example South America) as well as areas with a high number of emission sites and few nearby geological storage options (for example the Indian sub continent). This map however, does not address the relative capacity of any of the given sites to match, be it either a large emission supply or a small storage capacity. Neither does it address any of the technical uncertainties that could exist at any of the

storage sites or cost implications of the emission source due to the nature of the emission plant or the purity of the emission sources. Such issues of detailed source to store matching are dealt with in Chapter 5.

Figure 2.5. Geographical relationship between CO_2 emission sources and potential geological storage sites. The dots indicate CO_2 emission sources of 0.1 – 50 $MtCO_2$/yr. Prospectivity is a qualitative assessment of the likelihood that a suitable storage location is present in a given area based on the available information. Being only a perception it will change over time and with new information.

Figures 2.6, 2.7 and 2.8 show the regional emission clusters for 12 regions of the world, the available storage opportunities within each region, and compares the relative ranking of the area of available prospective sedimentary basins within a 300 km radius of emission clusters (Bradshaw and Dance, 2004). The 300 km radius was selected because it was considered to represent a significant transportation distance that can be used as a guide for likely transport distances for potentially viable source to storage matches (see Chapter 5). Although trends might be suggested from these data, such as high emissions for China with low area of prospective sedimentary basins, or high area of prospective sedimentary basin with low emissions for the Middle East, until detailed assessments are made in each region as to the quality and viability of each sedimentary basin and specific proposed sites, it is premature to make too many assumptions. Each basin will have its own technical peculiarities, and because the science of injection and storage of very large volumes of CO_2 is still developing, it is premature at this stage to make any substantive comments about the viability of individual sedimentary basins unless detailed data sets and assessments exist (see Chapter 5). These maps do, however, indicate where such detailed geological assessments will be required, such as China and India, before a comprehensive assessment can be made of the likely worldwide impact of geological storage of CO_2. These maps also show that CO_2 storage space is a resource, just like any other resource, and some regions will have many favourable opportunities, and others will not be so well endowed (Bradshaw and Dance, 2004).

Figure 2.6. Regional emission clusters, using 300 km buffer, relative to world geological storage prospectivity (Bradshaw and Dance, 2004).

Figure 2.7. Regional storage opportunities determined by using a ratio (percentage) of all prospective areas to non-prospective areas within a 300km buffer of major stationary emissions. The Pie Charts display the proportion of the prospective areas (sedimentary basins) that exists within the buffer regions (Bradshaw and Dance, 2004).

Figure 2.8. Proximity of emissions to sedimentary basins.

Figure 2.9 shows those emission sources with high concentration (>95%) CO_2, with their proximity to prospective geological storage sites. Clusters of high concentration sources can be observed in China and North America and to lesser extent in Europe.

Figure 2.9. Geographical relationship between high concentration CO_2 emission sources (> 95 %) with their proximity to prospective geological storage sites.

Ocean storage and source location matching

Due to an absence of publicly available literature a review of the proximity of large CO_2 point source emissions and their geographical relationship to ocean storage opportunities on the global scale could not be undertaken. A related study has been undertaken that analysed seawater

scrubbing of CO_2 from power stations along the coastlines of the world. The study considered the number of large stationary emission sources (in this case power generation plants) that exist on the coastline worldwide that would lie within 100 km of the 1500 m ocean floor contour (IEA GHG, 2000a). Eighty-nine potential power generation sources were identified that were proximate to these deep water locations. This number represents only a small proportion (>2%) of the total number of large stationary sources from the power generation sector worldwide (see Section 2.1). A greater proportion of power plants could potentially avail themselves of deep ocean storage because transport greater than 100 km may prove cost-effective in some cases; nevertheless, this study indicates that a greater fraction of large stationary sources could be more cost-effectively matched to geological storage reservoirs than ocean storage sites." There are many issues that will also need to be addressed when considering deep ocean storage sites, including jurisdictional boundaries, site suitability, and environmental impacts etc, which are discussed in Chapter 6. The spatial and temporal nature of ocean water column injection may impact on how such source and storage location matching are considered, as the CO_2 will not remain adjacent to the local region where the CO_2 is injected, and conceivably might migrate across jurisdictional boundaries and into sensitive environmental provinces.

2.5 Alternative energy carriers and CO_2 source implications

As discussed earlier in this chapter, a significant fraction of the world's CO_2 emissions comes from transportation, residences, and other small, distributed combustion sources. Whilst it is currently not economically feasible to capture and store CO_2 from these small, distributed sources, these emissions could be reduced if the fossil fuels used in these units were replaced with either:

- carbon-free energy carriers (e.g. electricity or hydrogen),
- energy carriers that are less carbon-intensive than conventional hydrocarbon fuels (e.g. methanol, Fischer-Tropsch liquids or dimethyl ether)
- biomass energy that can either be used directly or to produce energy carriers like bioethanol. If the biomass is grown sustainably the energy produced can be considered as carbon neutral.

In the first two cases, the alternative energy carriers can be produced in centralized plants that incorporate CO_2 capture and storage. In the case of biomass CO_2 capture and storage can also be incorporated into the energy carrier production schemes. The aim of this section is to explore the implications that introducing such alternative energy carriers and energy sources might have on future large point emissions sources of CO_2.

2.5.1 Carbon-free energy carriers

2.5.1.1 Electricity

The long-term trend has been toward electrification of the energy economy, and this trend is expected to continue (IPCC, 2000). To the extent that expanded electricity use is as a substitute for direct use of fossil fuels (e.g., in transportation or for cooking or heating applications in residences), the result can be less CO_2 emissions if the electricity is from carbon-free primary energy sources (renewable or nuclear) or from distributed generators such as fuel cells powered by hydrogen produced with near zero fuel cycle-wide emissions or from large fossil fuel power plants at which CO_2 is captured and stored.

Whilst in principle all energy could be provided by electricity, most energy projections envision that for many applications direct use of fuels will be preferred (IPCC, 2000). In transportation, for example, despite intensive developmental efforts, battery-powered electric vehicles have not

evolved beyond niche markets because the challenges of high cost, heavy weight, and long recharging times have not been overcome. Whilst currently available hybrid electric vehicles (which combine fossil fuel and electric batteries) seem to have good prospects for penetrating mass markets, these do not require charging from centralized electrical grids. Successful development of "plug-in hybrids" might lead to an expanded role for electricity in transportation, but such vehicles would still require fuel as well as grid electricity. In summary, it is expected that although electricity's share of total energy might continue to grow, most growth in large emission point CO_2 sources will be the result of increased primary energy demand.

2.5.1.2 Hydrogen

If hydrogen can be successfully established in the market as an energy carrier, a consequence could be the emergence of large new concentrated sources of CO_2, if the hydrogen is manufactured from fossil fuels in large pre-combustion decarbonization plants with CO_2 capture and storage. Such plants produce a high concentration source of CO_2 (see Chapter 3 for details on system design). Where fossil fuel costs are low and CO_2 capture and storage is feasible, hydrogen manufactured in this way is likely to be less costly than hydrogen produced from renewable or nuclear primary energy sources (Williams, 2003; NRC, 2004). It is noted that this technology can be utilized only if production sites are within a couple hundred kilometres of where the hydrogen will be used, since cost effective, long-distance hydrogen transportation represents a significant challenge. Producing hydrogen from fossil fuels can provide a technological development step towards a hydrogen economy based on carbon-free primary energy sources through the establishment of a hydrogen utilization infrastructure (Simbeck, 2003).

Energy market applications for hydrogen include its conversion to electricity electrochemically (in fuel cells) and in combustion applications. Substituting hydrogen for fossil fuel burning eliminates CO_2 emissions at the point of energy use. Much of the attention for hydrogen market development has been focused on distributed stationary applications in buildings and on transportation. Fuel cells are one option for use in stationary distributed energy (SDE) systems at scales as small as apartment buildings and even single-family residences (Lloyd, 1999). In building applications, hydrogen could also be combusted for heating and cooking (Ogden and Williams, 1989). In the transport sector, the hydrogen fuel cell car is the focus of intense development activity, with commercialization targeted for the middle of the next decade by several major auto manufacturers (Burns et al., 2002). For fuel cell vehicles, the main technological obstacles to widespread use are the current high costs of fuel cell vehicles and the bulkiness of compressed gaseous hydrogen storage (the only fully proven hydrogen storage technology), which restricts range between refuelling (NRC, 2004). However, currently achievable ranges might be acceptable to many consumers even without storage technology breakthroughs (Ogden et al., 2004).

Hydrogen might also be used in internal combustion engine (ICE) vehicles before fuel cell vehicles become available (Owen and Gordon, 2002), though efficiencies are likely to be less than with fuel cells. In this case the range between refuelling would also be less than for hydrogen fuel cell vehicles with the same performance (Ogden et al., 2004). For power generation applications, gas turbines originally designed for natural gas operation can be re-engineered to operate on hydrogen (Chiesa et al, 2003).

Currently there are a number of obstacles on the path to a hydrogen economy which are: the absence of cost-competitive fuel cells and other hydrogen using equipment and the absence of an infrastructure for getting hydrogen to consumers. These challenges are being addressed in many hydrogen R&D programs and policy studies being carried out around the world (Sperling and Cannon, 2004). There are also safety concerns because hydrogen has a wide flammability and

detonation limit, a low ignition energy, and high flame speed compared to other fuels. However, industrial experience shows that hydrogen can be manufactured and used safely in many applications (NRC, 2004).

There is widespread industrial experience with the production and distribution of hydrogen, mainly for synthesis of ammonia fertilizer and oil refinery hydro treating. Current global hydrogen production is 45 million t/yr, equivalent to 1.4% of global primary energy use in 2000 (Simbeck, 2003). Forty eight percent is produced from natural gas, 30% from oil, 18% from coal, and 4% via electrolysis of water. Ammonia production, which consumes about 100,000 MW_t of hydrogen, is growing 2-4% per year. Oil refinery demand for hydrogen is also growing, largely because of the ongoing shift to heavier crude oils and regulations limiting the sulphur content of transportation fuels. Most hydrogen is currently manufactured via steam methane reforming (SMR), steam reforming of naphtha, and gasification of petroleum residues and coal. The SMR option is generally favoured due to its lower capital cost wherever natural gas is available at reasonable prices. Nevertheless, there are currently about 75 modern commercial gasification plants making about 20,000 MW_t of hydrogen from coal and oil refinery residues (NETL-DOE, 2002); these are mostly ammonia fertilizer plants and oil refinery hydrogen plants in China, Europe, and North America. There are currently over 16,000 km of hydrogen pipelines around the world. Most are relatively short and located in industrial areas for large customers who make chemicals, reduce metals, and hydro treat oil at refineries. The longest pipeline currently in operation is 400 km and is located in a densely populated area of Europe, running from Antwerp to northern France. The pipeline operates at a pressure of about 60 atmospheres (Simbeck, 2004).

Fossil fuel plants producing hydrogen with CO_2 capture and storage would typically be large, producing, of the order 1000 MW_t (720 tonnes/day)[6] in order to keep the hydrogen costs and CO_2 storage costs low. Per kg of hydrogen, the co-production rate would be about 8 kg CO_2 with SMR and 15 kg CO_2 with coal gasification, so that the CO_2 storage rates (for plants operated at 80% average capacity factor) would be 1.7 and 3.1 million tonnes per year for SMR and coal gasification plants, respectively.

Making hydrogen from fossil fuels with CO_2 capture and storage in a relatively small number of large plants for use in large numbers of mobile and stationary distributed applications could lead to major reductions in fuel cycle wide emissions relative to petroleum based energy systems. This takes into account all fossil fuel energy inputs, including energy for petroleum refining and hydrogen compression at refuelling stations (NRC, 2004; Ogden et al., 2004). Estimates of the number of large stationary, concentrated CO_2 sources that could be generated via such hydrogen production systems and their geographical distribution have not yet been made.

2.5.2 Alternative energy carriers and CO_2 source implications

Interest in synthetic liquid fuels stems from concerns about both oil supply security (TFEST, 2004) and the expectation that it could possibly be decades before hydrogen, can make a major contribution to the energy economy (NRC, 2004).

There is considerable activity worldwide relating to the manufacture of Fischer-Tropsch liquids from stranded natural gas supplies. The first major gas to liquids (GTL) plant, producing 12,500 barrels per day, was built in Malaysia in 1993. Several projects are underway to make Fischer-Tropsch liquid fuels from natural gas in Qatar at plant capacities ranging from 30,000 to 140,000

[6] Such a plant operated at 80% capacity factor could support 2 million hydrogen fuel cell cars having a gasoline-equivalent fuel economy is 2.9 l/100 km and driven 14,000 km per year.

barrels per day. Although GTL projects typically do not produce concentrated by-product streams of CO_2, synthetic fuel projects using synthesis gas derived from coal (or other solid feedstocks such as biomass or petroleum residuals) via gasification could produce large streams of concentrated CO_2 that are good candidates for capture and storage. At Sasol in South Africa, coal containing some 20 million tonnes of carbon is consumed annually in the manufacture of synthetic fuels and chemicals. About 32% of the carbon ends up in the products, 40% is vented as CO_2 in dilute streams, and 28% is released as nearly pure CO_2, at a rate of about 20 million tonnes of CO_2 per year. Also, since 2000, 1.5 million tonnes per year of CO_2 by-product of synthetic methane production from a coal gasification plant in North Dakota (United States) has been captured and transported by pipeline 300 km to the Weyburn oil field in Saskatchewan (Canada), where it is used for enhanced oil recovery (see Chapter 5 for more details). Coal-based synthetic fuel plants being planned or considered in China; include six 600,000 t/yr methanol plants, two 800,000 t/yr dimethyl ether plants, and two or more large Fischer-Tropsch liquids plants.[7] In the United States, the Department of Energy is supporting a demonstration project in Pennsylvania to make 5,000 barrels/day of Fischer-Tropsch liquids plus 41 MW_e of electricity from low-quality coal.

If synthesis gas based energy systems become established in the market, economic considerations are likely to lead, as in the case of hydrogen production, to construction of large facilities that would generate huge relatively pure CO_2 co-product streams. Polygeneration plants, e.g. plants that could produce synthetic liquid fuels plus electricity, would benefit, as a result of economies of scale, economies of scope, and opportunities from greater system operating flexibility (Williams et al., 2000; Bechtel et al., 2003; Larson and Ren, 2003; Celik et al., 2005). In such plants, CO_2 could be captured from shifted synthesis gas streams both upstream and downstream of the synthesis reactor where the synthetic fuel is produced.

With CO_2 capture and storage, the fuel cycle wide greenhouse gas emissions per GJ for coal derived synthetic fuels can sometimes be less than for crude oil-derived fuels. For example, a study of DME manufacture from coal with CO_2 capture and storage found that fuel-cycle-wide greenhouse gas emissions per GJ ranged from 75 to 97% of the emission rate for diesel derived from crude oil, depending on the extent of CO_2 capture (Celik et al., 2005).

The CO_2 source implications of making synthetic low-carbon liquid energy carriers with CO_2 capture and storage are similar to those for making hydrogen from fossil fuels: large point source quantities of concentrated CO_2 would be available for capture. Again, estimates on the number of large stationary sources that could be generated and their geographical distribution have not yet been made.

2.5.3 CO_2 source implications of biomass energy production

There is considerable interest in some regions of the world in the use of biomass to produce energy, either in dedicated plants or in combination with fossil fuels. One set of options with potentially significant but presently uncertain implications regarding future CO_2 sources is bioenergy with CO_2 capture and storage. Such systems could be characterized by negative CO_2 emissions. The perceived CO_2 emission benefits and costs for such systems are discussed elsewhere in this report (see Chapters 3 and 8.) and are not further considered here. The aim of this section is to assess the current scale of emissions from biomass energy production and consider how they might vary in the future and thus consider their impact on the future number of, and scale of, CO_2 emissions sources.

[7] Most of the methanol would be used mainly for making chemicals and for subsequent conversion to dimethyl ether, although some methanol will be used for transportation fuel. The dimethyl ether would be used mainly as a cooking fuel.

2.5.3.1 Bioethanol production

Bioethanol is the main biofuel being produced today. Currently the two largest producers of bioethanol are the USA and Brazil. The USA produced 11 billion litres in 2003 nearly double the capacity in 1995. Production is expected to continue to rise because of government incentives. Brazilian production was over 14 billion litres per year in 2003 to 2004, similar to the level in 1997 to1998 (Möllersten et al 2003). Bioethanol is used directly in internal combustion engines, without modification, as a partial replacement for petroleum based fuels (5 to 10% replacement is used in Europe and USA).

Bioethanol plants are a high concentration source of CO_2 at atmospheric pressure that can be captured and subsequently stored. As can be seen in Table 2.3 the numbers of these plants is significant in the context of high purity sources, although their global distribution is restricted. These sources are comparable in size to those from ethylene oxide plants but smaller than those from ammonia plants.

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Although the trend in manufacture is to larger production facilities, the scale of future production will be determined by issues such as improvements in biomass production and conversion technologies, competition with other land use, water demand, markets for by-product streams and competition with other transport fuels.

Based on currently available literature, it is not possible to estimate the number of bioethanol plants that will be built in the future and the likely size of their CO_2 emissions.

2.5.3.2 Biomass as a primary energy source

A key issue posed by biomass energy production, both without and with CO_2 capture and storage is that of size. Current biomass energy production plants are much smaller than fossil fuel power plants, typical plant capacities are ~ 30 MW_e, with CO_2 emissions of less than 0.2 $MtCO_2$ per year. The size of these biomass energy production plants reflects the availability and dispersed nature of current biomass supplies, which are mainly crop and forestry residues.

The prospects for biomass energy production with CO_2 capture and storage might be improved in the future if economies of scale in energy production and/or CO_2 capture and storage could be realized. If, for instance, a CO_2 pipeline network is established in a country or region, then small CO_2 emission sources (including those from biomass energy plants) could be added to any nearby CO_2 pipelines if it economically viable to do so. A second possibility is that existing large fossil fuel plants with CO_2 capture and storage represent an opportunity for the co-processing of biomass. Co-processing biomass at coal power plants is already undertaken in a number of countries. However, it must be noted that if biomass is co-processed with a fossil fuel, these plants do not represent new large-scale emissions sources. A third possibility is to build larger biomass energy production plants than typical existing plants. Larger biomass energy production plants have been built or are being planned in a number of countries, typically those with extensive biomass resources. For example, Sweden already has seven biomass combined heat and plants at pulp mills that each produce around 130 MW_e equivalent. The size of biomass energy production plants is dependent on local circumstances, in particular the availability of concentrated biomass sources; pulp mills and sugar processing plants offer such concentrated sources. Larger plants might also be favoured if there were a shift from the utilization of biomass residues to dedicated energy crops.

Several studies have assessed the likely size of future biomass energy production plants, but there is not agreement among all these studies on the scale issue. One study, cited in Audus and Freund (2004), surveyed 28 favoured sites using woody biomass crops in Spain and concluded that the average appropriate scale would be in the range 30 to 70 MW_e, on the basis of that transport

distances longer than the assumed 40 km maximum would render larger plants uneconomic. In contrast, another study based on dedicated energy crops in Brazil and the United States estimated that economies of scale outweigh the extra costs of transporting biomass over long distances. In the latter study plant capacities of hundreds of MW_e were assessed to be feasible (Marrison and Larson, 1995). Similar findings have been reached in some other studies (Dornburg and Faaij, 2001; Hamelinck and Faaij, 2002). A recent study, analyzing a variety of options including both electricity and synthetic fuel production, indicated that large plants processing ~ 1000 MW_{th} of biomass would tend to be preferred for dedicated energy crops in the United States (Greene et al., 2004).

The size of future emission sources from bioenergy options is dependent to a large degree on local circumstances and the extent to which economic forces and/or public policies will encourage development of dedicated energy crops. The projections of annual global biomass energy use rising from 12 - 60 EJ by 2020, to 70 - 190 EJ per year by 2050, and to 120-380 EJ by 2100 in the SRES Marker Scenarios (IPCC, 2000) show that many global energy modellers expect that dedicated energy crops may well become more and more important during the course of this century. Thus, if bioenergy systems prove to be viable at scales suitable for CO_2 capture and storage, then the negative emissions potential of biomass (see Chapter 8) might, during the course of this century, become globally important. However, it is currently unclear the extent to which it will be feasible to exploit this potential both because of the uncertainties about scale of bioenergy conversion and the extent to which dedicated biomass energy crops will play a role in the future energy economy.

In summary, based on the available literature, at this stage it is not possible, to estimate the number of biomass energy production plants that will be built in the future and the likely size of their CO_2 emissions.

2.6 Gaps in knowledge

Whilst it is possible to determine the year 2000 emission source data (CO_2 concentration and point source geographical location) with a reasonable degree of accuracy for most industrial sectors, it is more difficult to predict the future location of emission point sources. Whilst all projections indicate there will be a growth in CO_2 emissions determining the actual locations for new plant plants can only currently be done subjectively.

A detailed definition of the storage capacity for the world's sedimentary basins is required. Although capacity estimates have been made these do not yet constitute a full resource assessment. Such information is essential to better define the opportunities that exist to store the CO_2 generated from large emission point sources. Currently only a simplistic exercise can be undertaken based on the limited data on storage capacity currently available in sedimentary basins.

An analysis of the storage potential for large point source emissions in the ocean could not be undertaken because detailed mapping indicating the relationship between storage locations in the oceans and point source emissions has not yet been carefully assessed.

The chapter highlights the fact that fossil fuel based hydrogen production from large centralised plants will potentially result in the generation of more high concentration emission sources. However, it is not currently possible to predict with any accuracy the number of these point sources that will arise and when because of market development uncertainties for hydrogen as an energy carrier. For example, before high concentration CO_2 sources associated with hydrogen production for energy can be exploited; cost-effective end-use technologies for hydrogen (e.g., low temperature

fuel cells) must be readily available in the market place. In addition, it is expected that it will take decades to build a hydrogen infrastructure that will bring the hydrogen from large centralized sources (where CCS is practical) to consumers.

Synthetic liquid fuels production or the co-production of liquid fuels and electricity via gasification of coal or other solid feedstocks or petroleum residuals can also lead to the generation of concentrated streams of CO_2. It is unclear at the present time the extent to which such synthetic fuels will be produced as alternatives to crude oil-derived hydrocarbon fuels. The co-production options, which seem especially promising, require market reforms that make it possible to electricity co product at a competitive market price.

During the course of this century biomass energy systems might become significant new large CO_2 sources, but this depends on the extent to which bioenergy conversion will take place in large plants, and the global significance of this option may well depend critically on the extent to which dedicated energy crops are pursued.

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Tables

Table 2.1. Properties of candidate gas streams that can be input to a capture process. (Sources: Campbell et al., 2000; Gielen and Moriguchi, 2003; Foster Wheeler, 1998; IEA GHG, 1999; IEA GHG, 2002a).

Source	CO_2 concentration % vol (dry)	Pressure of gas stream Mpa[1]	CO_2 partial pressure MPa
CO_2 from fuel combustion			
• Power station flue gas:			
Natural gas fired boilers	7-10	0.1	0.007-0.010
Gas turbines	3-4	0.1	0.003-0.004
Oil fired boilers	11-13	0.1	0.011-0.013
Coal fired boilers	12-14	0.1	0.012-0.014
IGCC[2]: after combustion	12-14	0.1	0.012-0.014
• Oil refinery and petrochemical plant fired heaters	8	0.1	0.008
CO_2 from chemical transformations + fuel combustion			
• Blast furnace gas:			
Before combustion[3]	20	0.2-0.3	0.040-0.060
After combustion	27	0.1	0.027
• Cement kiln off-gas	14-33	0.1	0.014-0.033
CO_2 from chemical transformations before combustion			
• IGCC: synthesis gas after gasification	8-20	2-7	0.16-1.4

[1] 0.1 MPa = 1 bar.
[2] IGCC: Integrated gasification combined cycle.
[3] Blast furnace gas contains also significant amounts of carbon monoxide that could be converted to CO_2 using the so-called shift reaction.

Table 2.2. Typical Properties of gas streams that are already input to a capture process (Sources: Chauvel and Lefebvre, 1989; Maddox and Morgan, 1998; IEA GHG, 2002a).

Source	CO_2 concentration % vol	Pressure of gas stream MPa[1]	CO_2 partial pressure MPa
Chemical reaction(s)			
• Ammonia production[2]	18	2.8	0.5
• Ethylene oxide	8	2.5	0.2
• Hydrogen production[2]	15-20	2.2-2.7	0.3-0.5
• Methanol production[2]	10	2.7	0.27
Other processes			
• Natural gas processing	2-65	0.9-8	0.05-4.4

[1] 0.1 MPa = 1 bar
[2] The concentration corresponds to high operating pressure for the steam methane reformer

Table 2.3. Profile of worldwide large CO_2 stationary sources emitting more than 0.1 Mt CO_2 per year (Source: IEA GHG, 2002a).

Process	CO_2 concentration in gas stream% by vol.	Number of sources	Emissions ($MtCO_2$)	% of total CO_2 emissions	Cumulative total CO_2 emissions (%)	Average emissions/source ($MtCO_2$ per source)
CO_2 from Fossil Fuels or Minerals						
Power						
Coal	12 to 15	2,025	7,984	59.69	59.69	3.94
Natural gas	3	985	759	5.68	65.37	0.77
Natural gas	7 to 10	743	752	5.62	70.99	1.01
Fuel oil	8	515	654	4.89	75.88	1.27
Fuel oil	3	593	326	2.43	78.31	0.55
Other fuels[1]	NA	79	61	0.45	78.77	0.77
Hydrogen	NA	2	3	0.02	78.79	1.27
Natural gas sweetening						
	NA[2]	NA	50[3]	0.37	79.16	
Cement production						
Combined	20	1175	932	6.97	86.13	0.79
Refineries						
	3 to 13	638	798	5.97	92.09	1.25
Iron and steel industry						
Integrated steel mills	15	180	630[4]	4.71	96.81	3.50
Other processes[4]	NA	89	16	0.12	96.92	0.17
Petrochemical industry						
Ethylene	12	240	258	1.93	98.85	1.08
Ammonia: process	100	194	113	0.84	99.70	0.58
Ammonia: fuel combustion	8	19	5	0.04	99.73	0.26
Ethylene oxide	100	17	3	0.02	99.75	0.15
Other sources						
Non-specified	NA	90	33	0.25	100.00	0.37
		7,584	**13,375**	**100**		**1.76**
CO_2 from Biomass[5]						
Bioenergy	3 to 8	213	73			0.34
Fermentation	100	90	17.6			**0.2**

[1] Other gas, other oil, digester gas, landfill gas

[2] A relatively small fraction of these sources has high CO_2 concentration. In Canada, only 2 plants out of a total of 24 have high CO_2 concentration streams

[3.] Based on an estimate that considers that about half of the annual worldwide natural gas production contains CO_2 at concentrations of about 4% mol and that this CO_2 content is normally reduced from 4% to 2% mol (see Section 3.2.2)

[4] This amount corresponds to the emissions of those sources that have been individually identified in the reference database. The worldwide CO_2 emissions, estimated by a top-down approach, are larger than this amount and over 1 Gt (Gielen and Moriguchi, 2003).

[5] For North America and Brazil only. All numbers are for 2003, except for power generation from biomass and waste in North America, which is for 2000

Table 2.4. Sectoral and regional distribution of energy-related CO_2 emissions in 2000 (Mt CO_2). (Source: IEA, 2003).

		Public Electricity and Heat Production	Unallocated Autoprodu-cers	Other Energy Industries	Manufacturing Industries and Construction	Transport	Commercial and Public Services	Residential	Other sectors	CO_2 Sectoral Approach Total
1	Economies in transition	1,118.5	391.4	106.6	521.7	317.1	58.0	312.5	127.7	2,953.6
2	OECD West	1,087.3	132.0	222.8	722.1	1,040.9	175.1	494.6	96.2	3,971.0
3	USA	2,265.1	134.9	272.4	657.9	1,719.9	225.5	371.4	42.7	5,689.7
4	OECD Pacific	509.2	87.0	62.2	301.1	344.4	95.3	75.8	35.7	1,510.5
5	South/east Asia	925.5	104.1	137.9	533.3	451.8	50.9	185.6	39.7	2,428.7
6	Centrally Planned Asia	1,332.2	37.7	138.5	978.4	245.4	72.6	221.4	118.7	3,144.8
7	Middle East	280.6	6.6	118.6	193.0	171.6	16.6	90.8	112.5	990.4
8	Africa	276.3	15.9	40.2	137.7	143.5	5.0	44.5	34.8	697.8
9	Latin America	222.3	37.0	134.5	279.3	396.0	17.9	81.0	41.5	1,209.6
	Sector total	8,016.9	946.5	1,233.7	4,324.7	4,830.6	716.8	1,877.5	649.4	22,596.1

Table 2.5. Carbon dioxide emissions from sectors in major world regions in six IPCC SRES scenarios in 2020 and 2050 (IPCC, 2000).

SOURCE: TOTAL EMISSIONS Mt CO_2 2020

A1B										
Sector	Africa	CPA	EEFSU	LAM	Middle East	USA	P-OECD	S&EA	OECD West	Sector total
Power	2,016	3,193	1,482	1,182	721	1,607	698	2,063	1,244	14,207
Industry	1,046	2,512	1,465	1,689	966	1,122	564	1,834	1,123	12,321
Res/Com	642	1,897	439	566	195	637	238	950	933	6,496
Transport	877	1,008	312	1,502	1,052	2,022	659	1,592	2,175	11,199
Region total	4,580	8,610	3,698	4,938	2,934	5,388	2,159	6,439	5,476	44,222

A1T												
Sector	SS-Africa	CPA	E Europe	FSU	LAM	ME-N Africa	NAM	P-OECD	PAS	SAS	W Europe	Sector total
Power	333	2,165	356	705	396	368	2,470	448	1,388	195	1,221	10,045
Industry	358	2,840	208	727	885	465	690	292	954	748	530	8,699
Res/Com	730	2,773	105	352	713	149	771	150	795	690	627	7,855
Refineries	107	211	23	196	282	139	370	75	250	42	219	1,913
Synfuels	59	122	9	22	139	36	127	30	211	38	107	900
Hydrogen	57	145	26	80	57	61	231	74	75	47	177	1,030
Transport	435	1,235	96	578	1,159	837	2,394	450	620	432	1,448	9,684
Region total	2,078	9,491	823	2,661	3,631	2,055	7,053	1,519	4,292	2,192	4,330	40,126

A1FI											
Sector	Africa	CPA	EEFSU	LAM	Middle East	USA	Canada	P-OECD	South East Asia	W Europe	Sector total
Power	427	3,732	2,248	680	370	2,618	181	753	2,546	1,640	15,195
Industry	622	3,498	1,121	695	426	1,418	153	416	1,530	1,384	11,262
Res/Com	135	1,363	582	125	25	755	102	115	488	786	4,477
Transport	456	542	588	977	297	2,210	168	357	1,357	1,345	8,297
Synfuels	10	12	126	2	0	52	3	12	2	21	238
Hydrogen	0	0	0	0	0	0	0	0	0	0	0
FuelFlared	21	11	19	135	74	9	1	1	52	4	327
Region total	1,670	9,159	4,682	2,613	1,192	7,062	608	1,654	5,976	5,181	39,796

Table 2.5. *Continued.*

SOURCE: TOTAL EMISSIONS Mt CO_2 2020

A2

Sector	Africa	East Asia	E Europe	FSU	LAM	Middle East	USA	Canada	P-OECD	South East Asia	South Asia	OECD Europe	Sector total
Power	670	1,616	488	923	1,130	857	3,680	224	689	356	1,282	1,663	13,579
Industry	290	1,786	261	417	625	402	808	111	291	218	708	528	6,444
Res/Com	269	746	118	539	209	434	639	92	155	87	251	644	4,181
Transport	358	606	130	314	1,060	569	2,013	200	406	334	332	1,270	7,592
Others	394	439	112	371	644	538	567	68	247	269	142	532	4,324
Region total	1,981	5,193	1,109	2,563	3,668	2,800	7,706	696	1,788	1,264	2,715	4,638	36,120

B1

Sector	Africa	East Asia	E Europe	FSU	LAM	Middle East	USA	Canada	P-OECD	South East Asia	South Asia	OECD Europe	Sector total
Power	629	1,148	377	670	1,031	699	2,228	128	477	354	972	1,118	9,829
Industry	259	1,377	210	290	531	362	537	79	205	209	611	355	5,024
Res/Com	283	602	108	471	193	350	511	74	132	79	250	557	3,611
Transport	384	578	136	343	987	509	1,708	172	365	314	370	1,204	7,070
Others	392	413	99	291	591	502	481	55	169	266	164	432	3,856
Region total	1,946	4,118	931	2,064	3,333	2,422	5,466	506	1,348	1,222	2,367	3,665	29,389

B2

Sector	SS-Africa	CPA	E Europe	FSU	LAM	ME-N Africa	NAM	P-OECD	PAS	SAS	W Europe	Sector total
Power	317	1,451	398	149	338	342	3,317	459	1,017	398	1,234	9,420
Industry	307	2,017	232	956	754	400	993	223	796	634	679	7,990
Res/Com	854	1,936	137	330	462	177	1,213	174	440	929	768	7,420
Refineries	70	241	42	169	223	193	480	98	242	111	271	2,139
Synfuels	30	18	2	32	47	16	126	4	77	12	56	420
Hydrogen	15	274	15	18	24	17	159	31	108	36	119	817
Transport	224	655	105	530	715	506	2,278	384	784	468	1,164	7,812
Region total	1,816	6,591	931	2,184	2,563	1,652	8,566	1,373	3,464	2,589	4,292	36,019

Table 2.5. *Continued.*

SOURCE: TOTAL EMISSIONS Mt CO_2 2050

A1B

Sector	Africa	CPA	EEFSU	LAM	Middle East	USA	P-OECD	S&EA	OECD West	Sector total
Power	4,078	2,708	1,276	1,165	840	1,361	588	2,700	1,459	16,174
Industry	2,304	2,555	1,645	2,384	1,635	969	395	3,273	1,038	16,199
Res/Com	2,610	3,297	879	1,074	415	797	236	2,056	1,004	12,369
Transport	4,190	2,082	512	2,841	2,676	2,091	690	4,506	2,278	21,867
Region total	13,182	10,643	4,311	7,465	5,566	5,218	1,909	12,535	5,779	66,609

A1T

Sector	SS-Africa	CPA	E Europe	FSU	LAM	ME-N Africa	NAM	P-OECD	PAS	SAS	W Europe	Sector total
Power	925	3,831	119	203	788	958	606	107	1,039	745	147	9,469
Industry	1,871	983	77	299	433	614	420	104	521	1,394	278	6,996
Res/Com	774	2,574	70	448	1,576	598	878	116	1,154	1,285	507	9,979
Refineries	71	477	12	395	314	299	263	32	287	137	42	2,330
Synfuels	811	442	137	118	699	22	715	114	515	339	418	4,329
Hydrogen	290	99	37	364	0	647	0	0	151	256	612	2,456
Transport	1,083	4,319	280	1,121	2,106	1,613	2,094	386	1,839	1,545	1,464	17,851
Region total	5,825	12,725	732	2,949	5,917	4,751	4,977	859	5,506	5,702	3,468	53,411

A1FI

Sector	Africa	CPA	EEFSU	LAM	Middle East	USA	Canada	P-OECD	South East Asia	W Europe	Sector total
Power	4,413	7,598	4,102	2,604	1,409	3,485	240	918	9,530	2,374	36,673
Industry	2,022	4,899	1,066	948	857	1,295	118	337	2,731	1,244	15,517
Res/Com	503	2,093	814	238	70	854	95	112	1,172	854	6,805
Transport	2,680	1,207	1,031	2,173	860	2,753	176	418	4,525	1,516	17,340
Synfuels	259	2,629	2,189	35	0	1,021	50	171	267	418	7,039
Hydrogen	0	0	0	0	0	0	0	0	0	0	0
FuelFlared	50	26	43	102	40	13	3	1	20	6	305
Region total	9,927	18,453	9,246	6,099	3,236	9,421	682	1,958	18,246	6,412	83,679

Table 2.5. *Continued.*

SOURCE: TOTAL EMISSIONS Mt CO_2 2050

A2													
Sector	Africa	East Asia	E Europe	FSU	LAM	Middle East	USA	Canada	P-OECD	South East Asia	South Asia	OECD Europe	Sector total
Power	2,144	3,406	913	1,679	2,621	2,518	4,653	310	1,028	967	3,660	1,766	25,666
Industry	881	2,727	345	725	1,118	899	895	115	276	413	1,627	487	10,506
Res/Com	907	1,451	157	735	325	719	644	95	144	179	599	628	6,582
Transport	1,061	901	193	646	1,547	1,370	1,946	191	378	578	703	1,275	10,788
Others	719	643	106	452	754	904	582	67	142	304	359	429	5,461
Region total	5,713	9,127	1,714	4,237	6,365	6,409	8,719	778	1,967	2,441	6,949	4,585	59,003

B1													
Sector	Africa	East Asia	E Europe	FSU	LAM	Middle East	USA	Canada	P-OECD	South East Asia	South Asia	OECD Europe	Sector total
Power	573	251	104	343	496	662	342	30	82	313	1,243	311	4,749
Industry	556	985	121	235	465	574	319	44	103	250	877	171	4,699
Res/Com	517	465	92	358	242	298	338	52	81	105	455	384	3,389
Transport	959	571	127	466	946	834	976	104	204	390	660	732	6,968
Others	414	280	45	209	378	458	230	29	60	198	253	225	2,779
Region total	3,019	2,551	488	1,612	2,527	2,825	2,205	259	529	1,255	3,488	1,824	22,584

B2												
Sector	SS-Africa	CPA	E Europe	FSU	LAM	ME-N Africa	NAM	P-OECD	PAS	SAS	W Europe	Sector total
Power	654	1,703	474	576	274	753	2,280	289	762	1,357	936	10,060
Industry	932	1,751	166	685	688	601	708	66	827	1,499	406	8,328
Res/Com	623	1,850	85	386	477	127	1,084	129	661	1,106	610	7,138
Refineries	43	360	14	409	200	85	382	47	244	262	112	2,157
Synfuels	453	139	56	285	326	448	174	50	223	54	97	2,304
Hydrogen	308	1,312	43	278	277	186	319	29	185	444	364	3,743
Transport	572	1,531	145	840	1,230	799	2,577	340	1,014	1,075	1,336	11,459
Region total	3,584	8,645	984	3,458	3,471	2,999	7,524	951	3,917	5,797	3,861	45,189

Notes:

The division of the world into large economic regions differs across different models underlying the SRES scenarios. Tables 2.5 and 2.6 consolidate the original model regions at a level that makes model results comparable (although the exact geographical coverage of the regions may vary). Acronyms and the associated regions can be found in Appendix II.

Table 2.6. Carbon dioxide emissions available for capture and storage from sectors in major world region in six IPCC SRES scenarios in 2020 and 2050 (Source: after Toth and Rogner, 2005).

Potential CO_2 capture in Mt CO_2 2020

A1B										
Sector	Africa	CPA	EEFSU	LAM	MEA	NAM	P-OECD	S&EA	OECD West	Sector total
Power	117	475	319	165	167	479	185	290	351	2,548
Industry	33	182	168	155	127	156	64	130	159	1,173
Res/Com	6	46	21	16	7	30	12	17	51	207
Transport	0	0	0	0	0	0	0	0	0	0
Region total	156	702	508	337	301	665	261	437	561	3,928

A1T												
Sector	SS-Africa	CPA	E Europe	FSU	LAM	ME-N Africa	NAM	P-OECD	PAS	SAS	W Europe	Sector total
Power	21	334	78	139	39	110	715	128	164	20	366	2,115
Industry	6	195	18	70	56	57	85	21	35	57	65	664
Res/Com	4	59	4	16	14	4	37	7	12	6	36	200
Refineries	22	54	6	50	71	42	113	23	63	11	67	521
Synfuels	30	74	6	16	85	25	91	23	86	16	81	532
Hydrogen	46	125	24	73	50	56	211	68	65	41	162	919
Transport	0	0	0	0	0	0	0	0	0	0	0	0
Region total	129	840	135	364	315	294	1,251	270	426	150	777	4,950

A1FI											
Sector	Africa	CPA	EEFSU	LAM	Middle East	USA	Canada	P-OECD	South East Asia	W Europe	Sector total
Power	30	607	525	95	90	791	55	226	401	500	3,319
Industry	15	259	144	49	58	189	22	51	104	198	1,091
Res/Com	1	31	26	4	1	36	4	6	7	48	165
Transport	0	0	0	0	0	0	0	0	0	0	0
Synfuels	5	7	89	1	0	37	2	9	1	16	167
Hydrogen	0	0	0	0	0	0	0	0	0	0	0
FuelFlared	0	0	0	0	0	0	0	0	0	0	0
Region total	50	904	785	149	149	1,053	83	292	513	763	4,741

Table 2.6. *Continued.*

Potential CO_2 capture in Mt CO_2 2020													
A2													
Sector	Africa	East Asia	E Europe	FSU	LAM	Middle East	USA	Canada	P-OECD	South East Asia	South Asia	OECD Europe	Sector total
Power	41	241	102	217	150	208	1,111	66	201	60	140	477	3,016
Industry	8	127	26	49	42	48	111	15	35	12	49	68	590
Res/Com	3	25	5	26	6	15	30	4	8	2	5	35	163
Transport	0	0	0	0	0	0	0	0	0	0	0	0	0
Others	0	0	0	0	0	0	0	0	0	0	0	0	0
Region total	51	392	134	292	198	271	1,252	86	244	74	194	579	3,769
B1													
Sector	Africa	East Asia	E Europe	FSU	LAM	Middle East	USA	Canada	P-OECD	South East Asia	South Asia	OECD Europe	Sector total
Power	38	156	81	160	147	174	632	35	126	57	129	304	2,040
Industry	6	79	19	32	35	43	68	10	22	10	45	43	411
Res/Com	3	22	5	22	5	11	22	3	6	2	5	28	134
Transport	0	0	0	0	0	0	0	0	0	0	0	0	0
Others	0	0	0	0	0	0	0	0	0	0	0	0	0
Region total	47	256	105	214	187	228	722	49	155	69	179	375	2,584
B2													
Sector	SS-Africa	CPA	E Europe	FSU	LAM	ME-N Africa	NAM		P-OECD	PAS	SAS	W Europe	Sector total
Power	18	225	82	24	52	100	982		114	153	41	349	2,140
Industry	5	122	19	89	42	50	103		12	19	30	73	565
Res/Com	5	42	5	15	6	4	46		8	6	6	35	178
Refineries	14	60	11	42	56	58	144		29	61	28	81	583
Synfuels	15	11	2	22	28	11	88		3	31	5	42	258
Hydrogen	12	233	14	16	20	16	144		28	92	31	107	712
Transport	0	0	0	0	0	0	0		0	0	0	0	0
Region total	69	693	132	209	204	239	1,507		196	361	140	687	4,437

Table 2.6. *Continued.*

Potential CO_2 Capture in Mt CO_2 2050											
A1B											
Sector	Africa	CPA	EEFSU	LAM	Middle East	NAM	P-OECD	S&EA	OECD West	Sector total	
Power	2,167	1,701	831	674	548	1,015	438	1,658	1,092	10,124	
Industry	760	931	726	1,015	701	439	165	1,201	481	6,419	
Res/Com	222	660	191	128	87	172	68	393	319	2,241	
Transport	0	0	0	0	0	0	0	0	0	0	
Region total	3,149	3,291	1,747	1,818	1,337	1,627	671	3,253	1,892	18,783	
A1T											
Sector	SS-Africa	CPA	E Europe	FSU	LAM	ME-N Africa	NAM	P-OECD	PAS	SAS	W Europe	Sector total
Power	526	2,530	90	127	469	753	477	84	702	423	115	6,296
Industry	329	307	25	110	165	191	139	33	111	288	102	1,799
Res/Com	66	445	16	94	189	126	190	32	238	140	159	1,694
Refineries	37	367	9	304	242	245	216	26	221	98	35	1,799
Synfuels	665	407	126	109	645	20	660	105	449	296	386	3,867
Hydrogen	283	96	36	354	0	630	0	0	147	249	596	2,392
Transport	0	0	0	0	0	0	0	0	0	0	0	0
Region total	1,905	4,154	301	1,098	1,709	1,965	1,681	280	1,867	1,493	1,393	17,846
A1FI											
Sector	Africa	CPA	EEFSU	LAM	Middle East	USA	Canada	P-OECD	South East Asia	W Europe	Sector total	
Power	2,369	4,836	2,691	1,486	992	2,677	186	705	5,979	1,862	23,781	
Industry	557	1,817	462	332	370	559	53	144	962	569	5,826	
Res/Com	37	430	188	27	15	189	23	30	229	279	1,448	
Transport	0	0	0	0	0	0	0	0	0	0	0	
Synfuels	213	2,425	2,019	32	0	942	46	158	233	385	6,453	
Hydrogen	0	0	0	0	0	0	0	0	0	0	0	
FuelFlared	0	0	0	0	0	0	0	0	0	0	0	
Region total	3,175	9,509	5,360	1,877	1,377	4,367	308	1,038	7,403	3,095	37,508	

Table 2.6. *Continued.*

Potential CO_2 Capture in Mt CO_2 2050													
A2													
Sector	Africa	East Asia	E Europe	FSU	LAM	Middle East	USA	Canada	P-OECD	South East Asia	South Asia	OECD Europe	Sector total
Power	1,158	2,080	571	1,110	1,407	1,628	3,569	230	779	631	1,912	1,284	16,359
Industry	257	991	128	286	365	319	384	46	112	139	519	194	3,741
Res/Com	78	293	34	155	41	148	143	21	42	30	113	197	1,295
Transport	0	0	0	0	0	0	0	0	0	0	0	0	0
Others	0	0	0	0	0	0	0	0	0	0	0	0	0
Region total	1,493	3,365	733	1,552	1,812	2,095	4,096	298	933	799	2,544	1,675	21,394
B1													
Sector	Africa	East Asia	E Europe	FSU	LAM	Middle East	USA	Canada	P-OECD	South East Asia	South Asia	OECD Europe	Sector total
Power	266	130	63	218	258	418	221	19	52	185	635	203	2,668
Industry	138	268	40	83	137	196	118	16	36	72	271	64	1,437
Res/Com	44	80	19	69	28	57	69	11	21	16	73	111	598
Transport	0	0	0	0	0	0	0	0	0	0	0	0	0
Others	0	0	0	0	0	0	0	0	0	0	0	0	0
Region total	447	478	121	371	423	671	408	46	110	273	980	377	4,703
B2													
Sector	SS-Africa	CPA	E Europe	FSU	LAM	ME-N Africa	NAM		P-OECD	PAS	SAS	W Europe	Sector total
Power	339	1,067	307	345	164	563	1,710		216	439	673	704	6,526
Industry	166	459	63	248	266	257	225		20	157	238	144	2,243
Res/Com	42	309	18	77	52	16	224		35	102	104	182	1,161
Refineries	22	270	11	306	150	68	305		38	183	183	89	1,625
Synfuels	362	125	51	256	293	403	157		45	189	46	87	2,015
Hydrogen	293	1,246	41	264	263	176	303		27	176	421	345	3,556
Transport	0	0	0	0	0	0	0		0	0	0	0	0
Region total	1,223	3,476	489	1,496	1,187	1,484	2,924		383	1,246	1,665	1,552	17,125

Notes:
The division of the world into large economic regions differs across different models underlying the SRES scenarios. Tables 2.5 and 2.6 consolidate the original model regions at a level that makes model results comparable (although the exact geographical coverage of the regions may vary). Acronyms and the associated regions can be found in Appendix II.

Figures

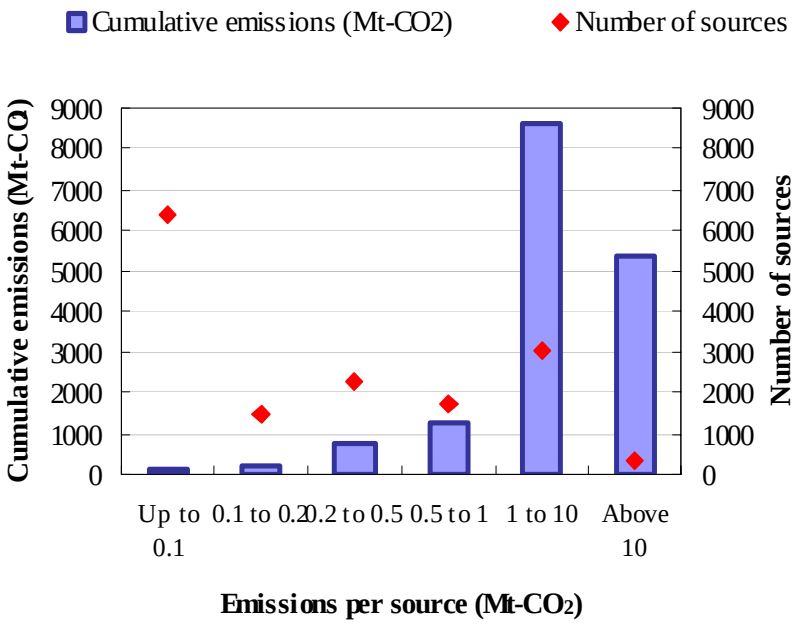

Figure 2.1. Relationship between large stationary source emissions and number of emission sources (*Source*: IEA GHG 2002a).

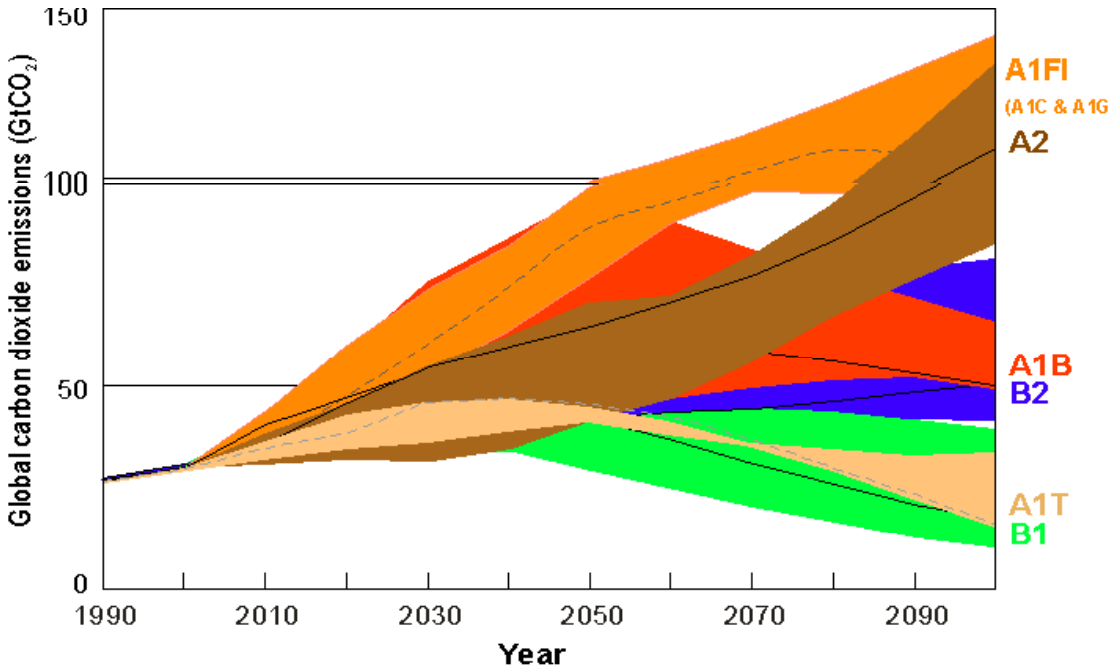

Figure 2.2. Range of annual global CO_2 emissions in the SRES scenarios (Source: IPCC, 2000).

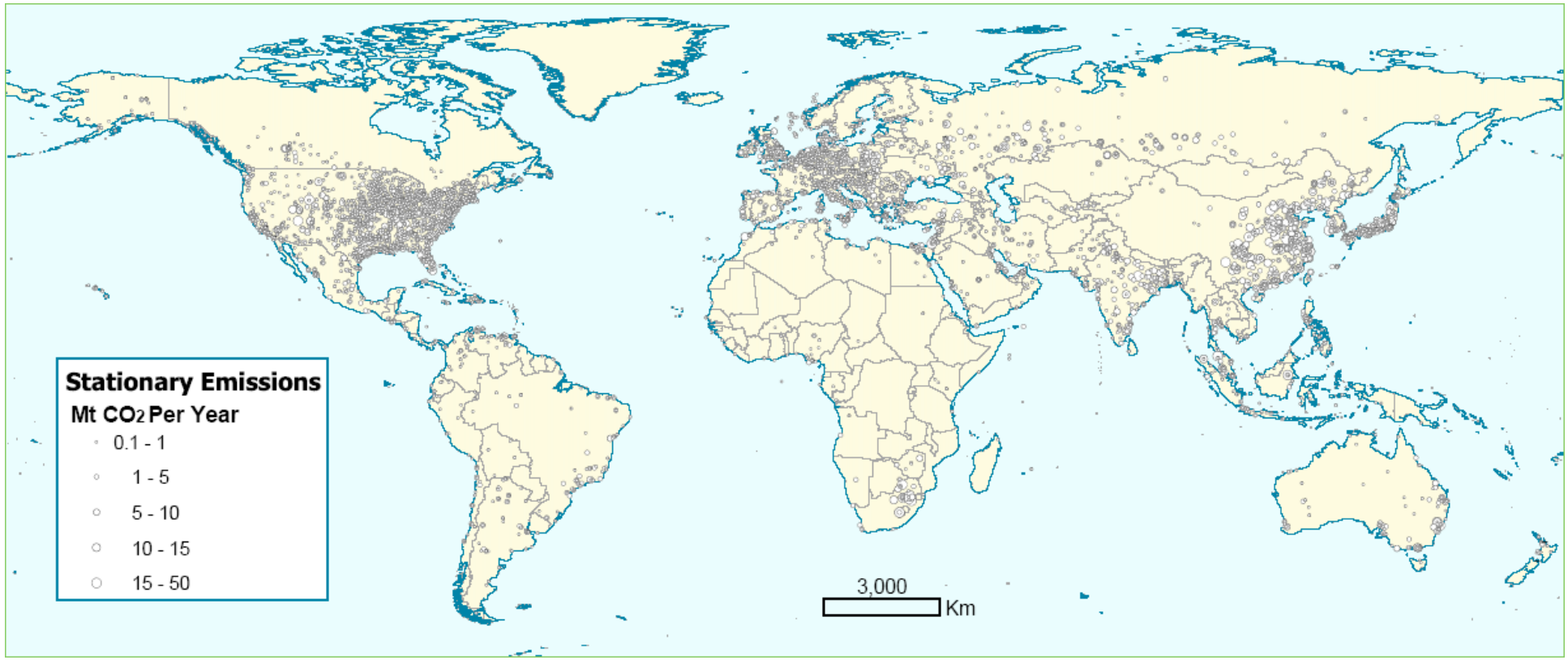

Figure 2.3. Global distribution of large stationary CO_2 sources (Source: IEA GHG, 2000a).

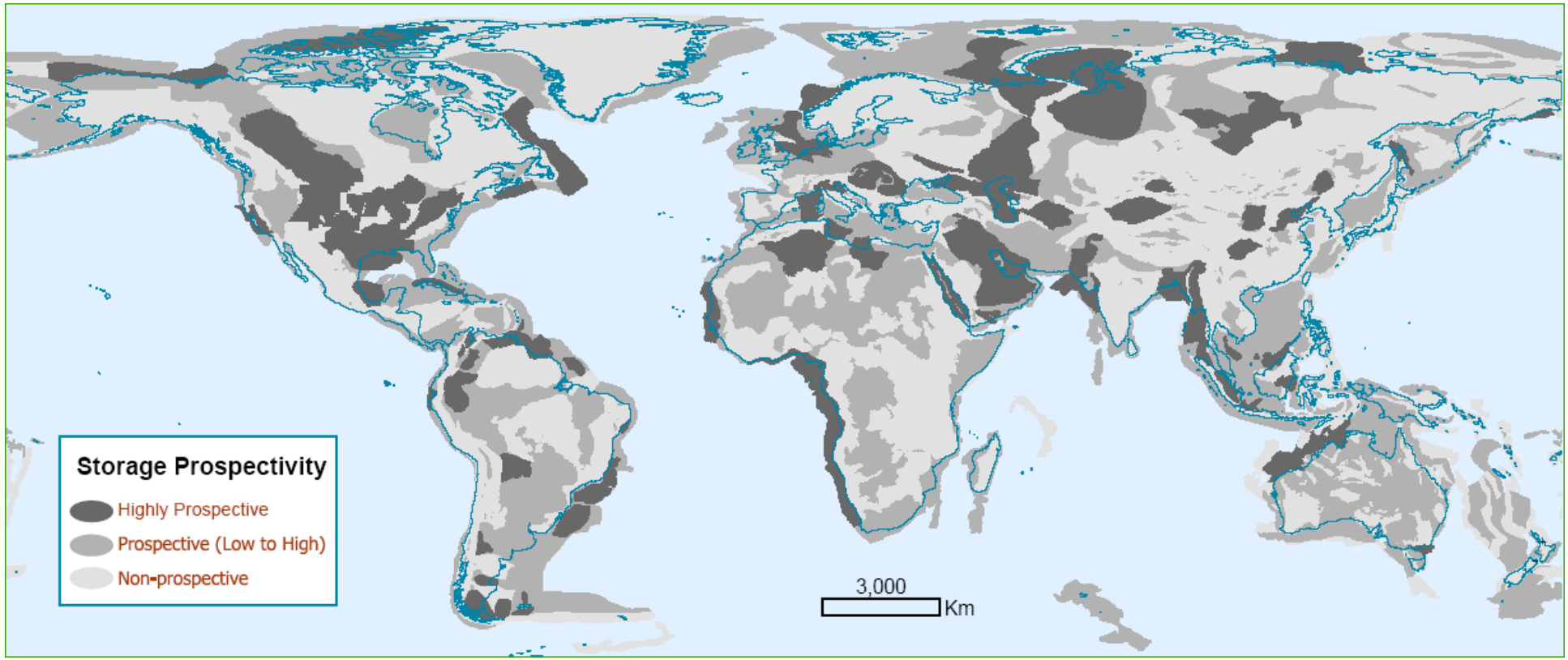

Figure 2.4. High-level estimate of the CO_2 geological storage potential for sedimentary basins of the world (Bradshaw and Dance 2004).

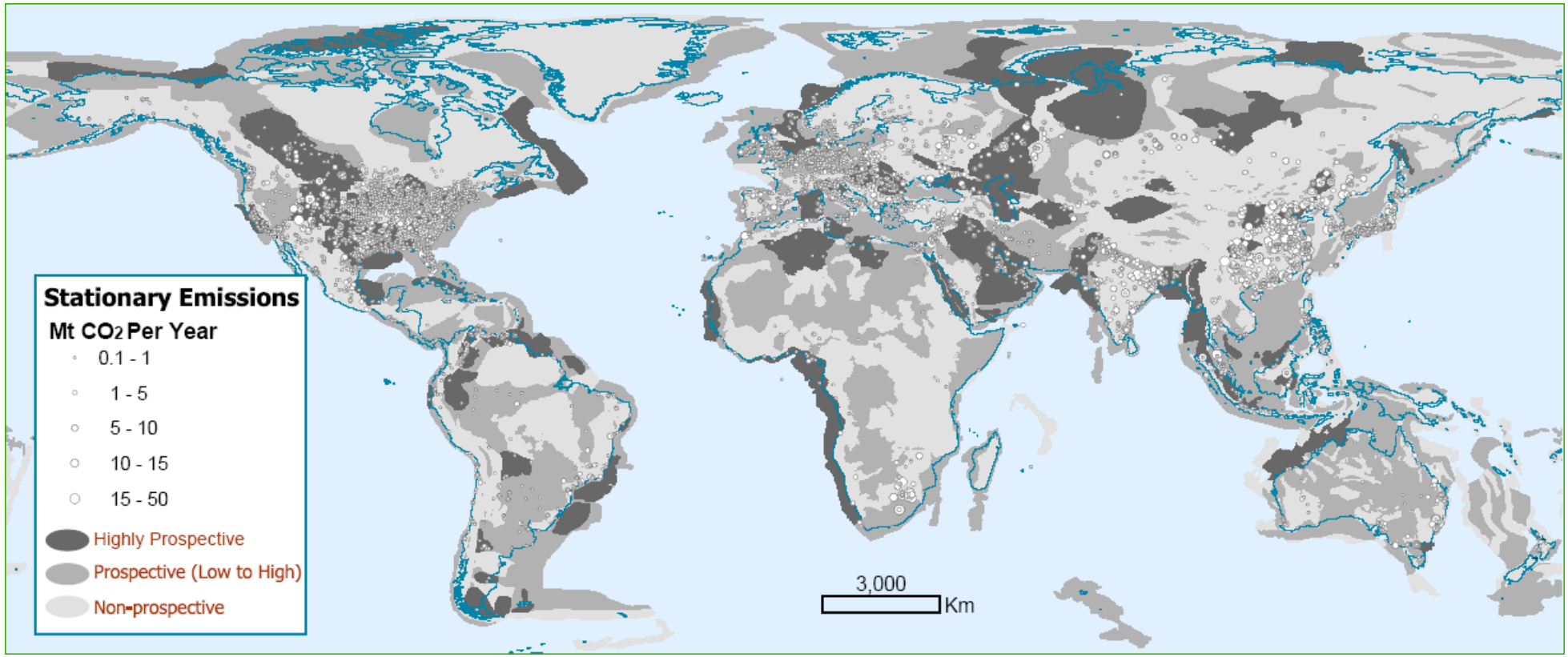

Figure 2.5. Geographical relationship between CO_2 emission sources and potential geological storage sites. The dots indicate CO_2 emission sources of 0.1 – 50 $MtCO_2/yr$. Prospectivity is a qualitative assessment of the likelihood that a suitable storage location is present in a given area based on the available information. Being only a perception it will change over time and with new information.

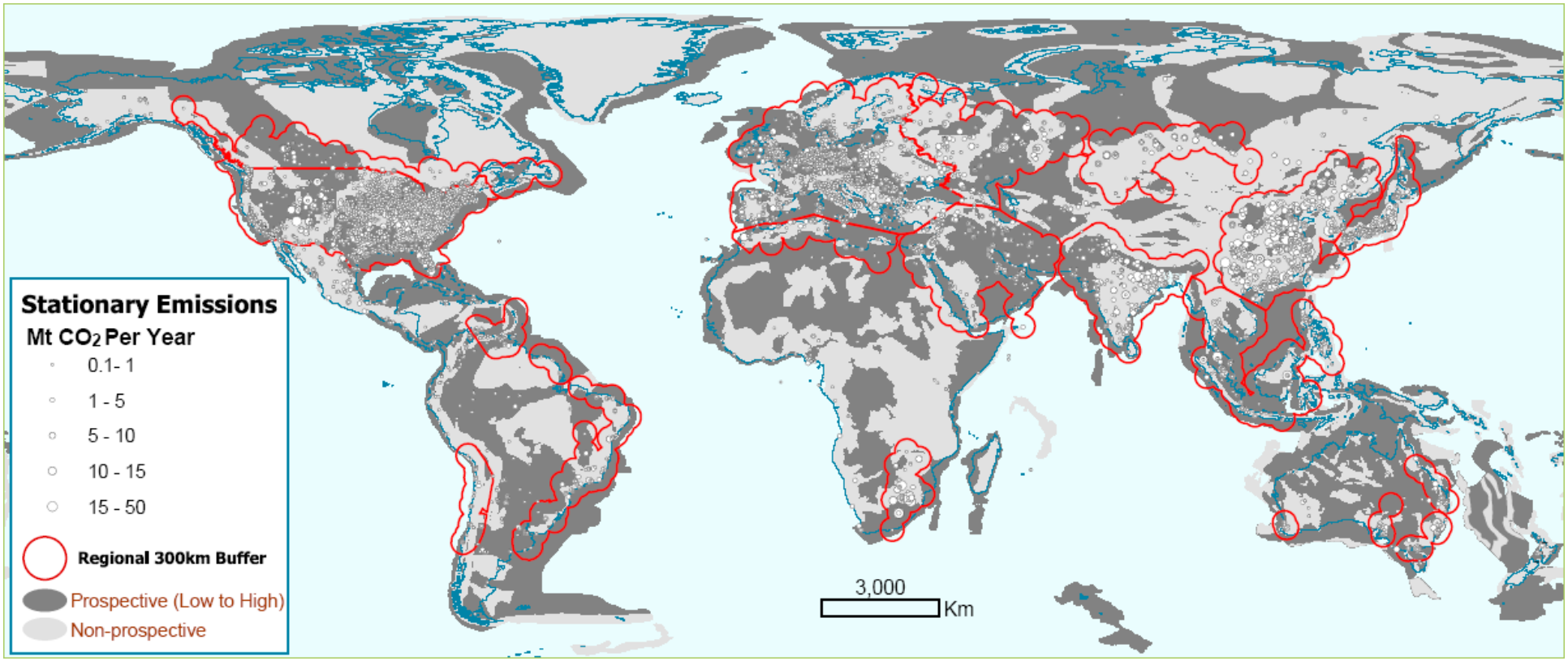

Figure 2.6. Regional emission clusters, using 300 km buffer, relative to world geological storage prospectivity (Bradshaw and Dance, 2004).

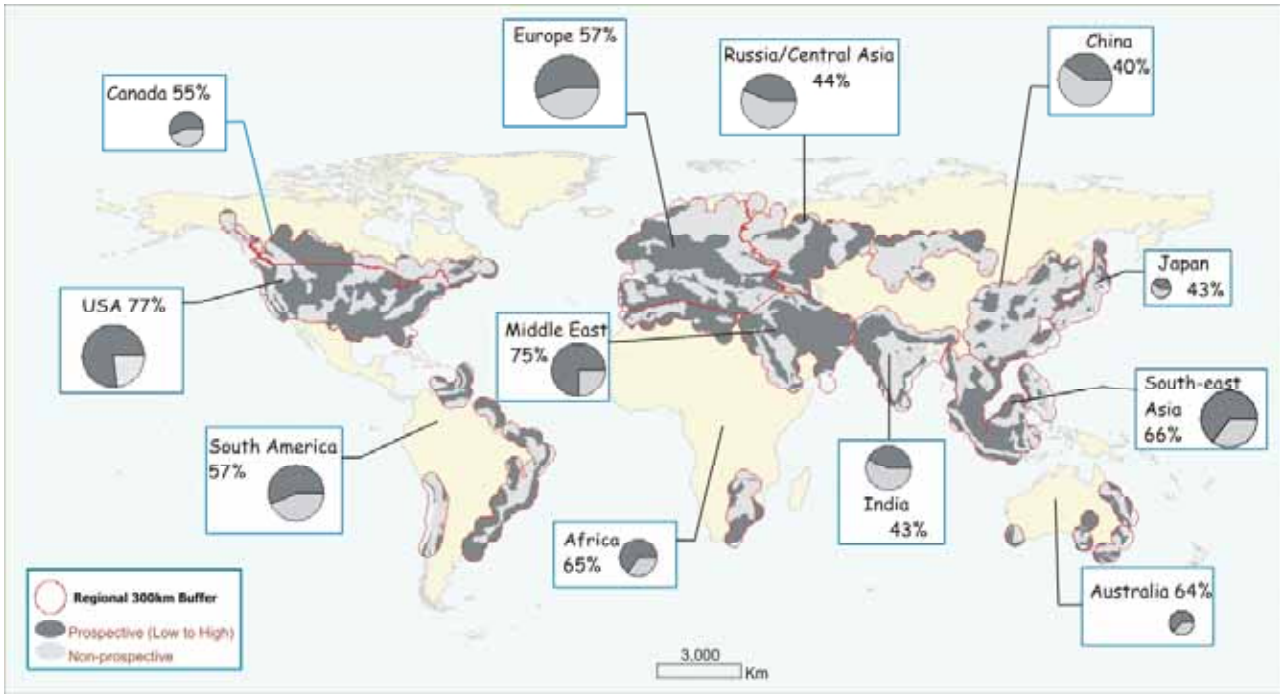

Figure 2.7. Regional storage opportunities determined by using a ratio (percentage) of all prospective areas to non-prospective areas within a 300km buffer of major stationary emissions. The Pie Charts display the proportion of the prospective areas (sedimentary basins) that exists within the buffer regions (Bradshaw and Dance, 2004).

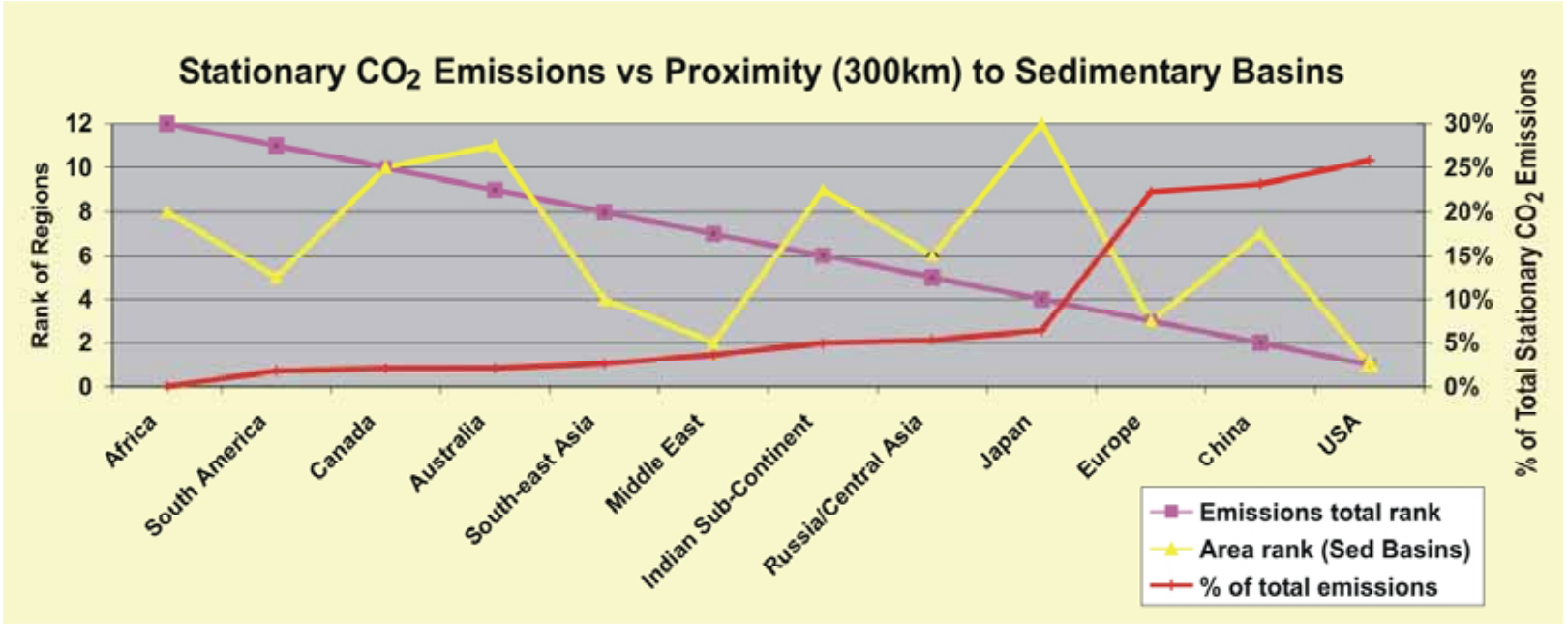

Figure 2.8. Proximity of emissions to sedimentary basins.

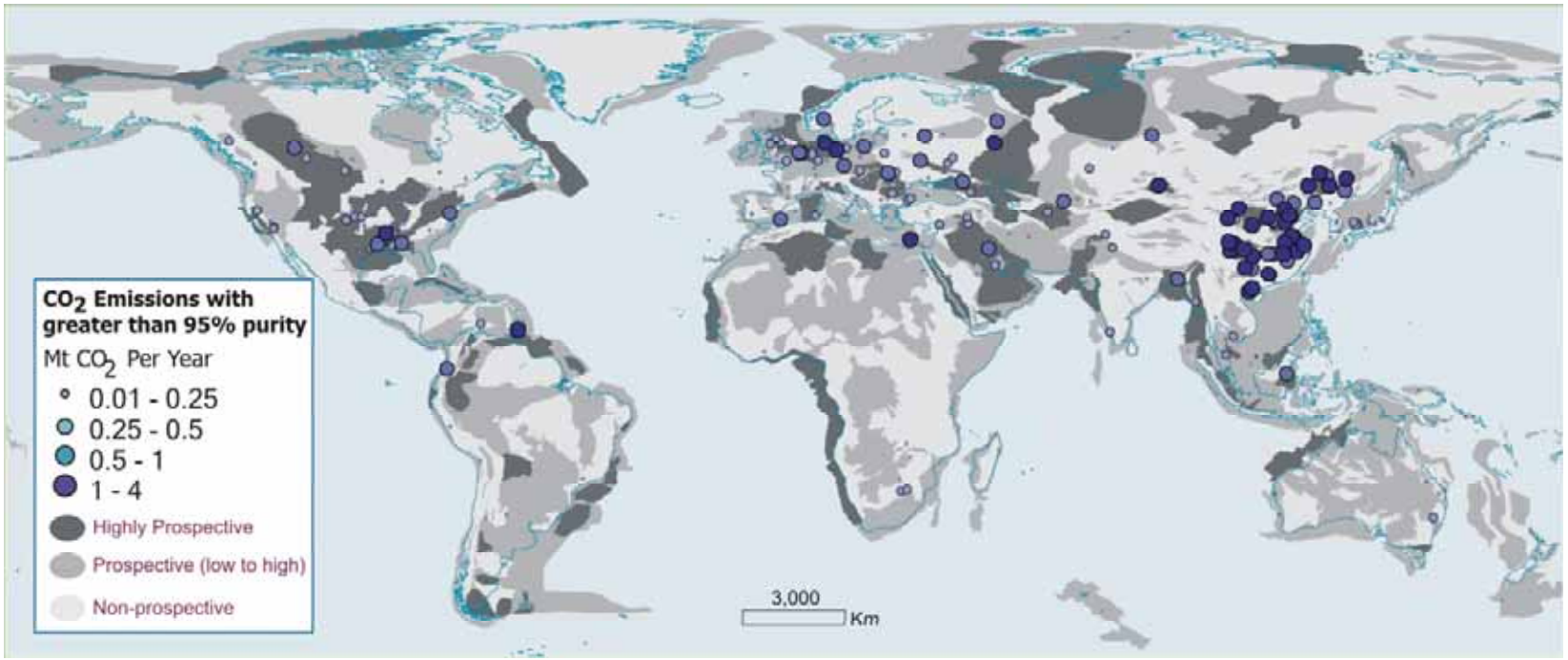

Figure 2.9. Geographical relationship between high concentration CO_2 emission sources (> 95 %) with their proximity to prospective geological storage sites.

5

3. Capture

Coordinating Lead Authors

KELLY (KAILAI) THAMBIMUTHU (AUSTRALIA and CANADA), MOHAMMAD SOLTANIEH (IRAN), JUAN CARLOS ABANADES (SPAIN)

Lead Authors

Rodney Allam (United Kingdom), Olav Bolland (Norway), John Davison (United Kingdom), Paul Feron (The Netherlands), Fred Goede (South Africa), Alyce Herrera (Phillippines), Masaki Iijima (Japan), Daniël Jansen (The Netherlands), Iosif Leites (Russian Federation), Philippe Mathieu (Belgium), Edward Rubin (United States), Dale Simbeck (United States), Krzysztof Warmuzinski (Poland), Michael Wilkinson (United Kingdom), Robert Williams (United States)

Contributing Authors

Manfred Jaschik (Poland), Anders Lyngfelt (Sweden), Roland Span (Germany), Marek Tanczyk (Poland)

Review Editors

Ziad Abu-Ghararah (Saudi Arabia), Tatsuaki Yashima (Japan)

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Executive Summary

The purpose of CO_2 capture is to produce a concentrated stream which can readily be transported to a CO_2 storage site. CO_2 capture and storage is most applicable to large, centralized sources like power plants and large industries. Capture technologies also open the way for large-scale production of low-carbon or carbon-free electricity and fuels for transportation, as well as for small-scale or distributed applications. The energy required to operate CO_2 capture systems reduces the overall efficiency of power generation or other processes, leading to increased fuel requirements, solid wastes, and environmental impacts relative to the same type of base plant without capture. However, as more efficient plants with capture become available and replace many of the older less efficient plants now in service, the net impacts will be compatible with clean air emission goals for fossil fuel use. Minimization of energy requirements for capture, together with improvements in the efficiency of energy conversion processes, thus remain as high priorities for future technology development in order to minimize overall environmental impacts and cost.

CO_2 is routinely separated today at some large industrial plants such as natural gas processing and ammonia production facilities, although these plants remove CO_2 to meet process demands and not for storage. CO_2 capture also has been applied to several small power plants. However, there have been no applications at large-scale power plants of several hundred megawatts that are the major source of current and projected CO_2 emissions. For industrial and power plant applications, there are three main approaches to CO_2 capture. *Post-combustion* systems separate CO_2 from the flue gases produced by combustion of a primary fuel (coal, natural gas, oil or biomass) in air. *Oxy-fuel combustion* uses oxygen instead of air for combustion, producing a flue gas that is mainly H_2O and CO_2 that is readily captured, and is an option still under development. *Pre-combustion* systems process the primary fuel in a reactor to produce separate streams of CO_2 for storage and H_2 which is used as a fuel. Other industrial processes, including processes for the production of low-carbon or carbon-free fuels, employ one or more of these same basic capture methods. The monitoring, risk and legal aspects associated with CO_2 capture systems appear to present no new challenges, as they are all elements of long-standing health, safety and environmental control practice in industry.

For all applications noted above, we reviewed recent studies of the performance and cost of commercial or near-commercial technologies, as well as that of newer CO_2 capture concepts that are the subject of intense R&D efforts worldwide. For power plants, current commercial CO_2 capture systems can reduce CO_2 emissions per kilowatt-hour (kWh) by 85-90%. Across all plant types the cost of electricity production (COE) increases by 12-36 US$/MWh (1.2-3.6 c/kWh) over a similar type of plant without capture, corresponding to a 40-85% increase for a supercritical pulverised coal (PC) plant, 35-70% for a natural gas combined cycle (NGCC) plant, and 20-55% for an integrated gasification combined cycle (IGCC) plant using bituminous coal. Overall, the COE for fossil fuel plants with capture ranges from 43-86 US$/MWh, with the cost per tonne of CO_2 ranging from 11-57 US$/tonne CO_2 captured or 13-74 US$/tonne CO_2 avoided (depending on plant type, size, fuel type, and a host of other factors). These costs include CO_2 compression but not additional transport and storage costs. NGCC systems typically have a lower COE than new PC and IGCC plants (with or without capture) for gas prices below about 4 US$/GJ. Most studies indicate that IGCC plants are slightly more costly without capture and slightly less costly with capture than similarly sized PC plants, but the differences in cost for plants with CO_2 capture can vary with coal type and other local factors. The lowest CO_2 capture costs (averaging about 12 US$/tonne captured or 15 US$/tonne CO_2 avoided) were found for industrial processes such as hydrogen production plants that produce concentrated CO_2 streams as part of the current production process; such industrial processes may represent some of the earliest opportunities for CCS. In all cases, CO_2 capture costs are highly dependent upon technical, economic and financial factors related to the design and operation of the production process or power system of interest, as well as the design

and operation of the CO_2 capture technology employed. Thus, comparisons of alternative technologies, or the use of CCS cost estimates, require a specific context to be meaningful.

New or improved methods of CO_2 capture, combined with advanced power systems and industrial process designs, can significantly reduce CO_2 capture costs and associated energy requirements. While there is considerable uncertainty about the magnitude and timing of future cost reductions, this assessment suggests that improvements to commercial technologies can reduce CO_2 capture costs by at least 20-30% over approximately the next decade, while new technologies under development promise more substantial cost reductions. Realization of future cost reductions, however, will require deployment and adoption of commercial technologies in the marketplace as well as sustained R&D.

3.1 Introduction

3.1.1 The basis for CO_2 capture

The main application of CO_2 capture is likely to be at large point sources: fossil fuel power plants, fuel processing plants, and other industrial plants, particularly for the manufacture of iron, steel, cement and bulk chemicals, as discussed in Chapter 2.

Capturing CO_2 directly from small and mobile sources in the transportation and residential and commercial building sectors is expected to be more difficult and expensive than from large point sources. Small-scale capture is therefore not discussed further in this chapter. An alternative way of avoiding emissions of CO_2 from these sources would be by use of energy carriers such as hydrogen or electricity produced in large fossil fuel based plants with CO_2 capture or by using renewable energy sources. Production of hydrogen with CO_2 capture is included in this chapter.

The possibility of CO_2 capture from ambient air (Lackner, 2003) is not discussed in this chapter because the CO_2 concentration in ambient air is around 380 ppm, a factor of 100 or more lower than in flue gas. Capturing CO_2 from air by the growth of biomass and its use in industrial plants with CO_2 capture is more cost effective based on foreseeable technologies and is included in this chapter.

It is implicit in analysis of possible future scenarios for anthropogenic greenhouse gas emissions that technological innovations will be one of the key factors which determines our future path (Section 2.5.3). For this reason this chapter deals not only with application of existing technology for CO_2 capture, but describes many new processes under development which may result in lower CO_2 capture costs in future.

3.1.2 CO_2 capture systems

There are four basic systems for capturing CO_2 from use of fossil fuels and/or biomass

- Capture from industrial process streams (described in Section 3.2)
- Post-combustion capture (described in Section 3.3)
- Oxy-fuel combustion capture (described in Section 3.4)
- Pre-combustion capture (described in Section 3.5)

These systems are shown in simplified form in Figure 3.1.

Figure 3.1. CO_2 capture systems (adapted from BP).

3.1.2.1 Capture from industrial process streams

CO_2 has been captured from industrial process streams for 80 years (Kohl and Nielsen, 1997), although most of the CO_2 that is captured is vented to the atmosphere because there is no incentive or requirement to store it. Current examples of CO_2 capture from process streams are purification of natural gas and production of hydrogen-containing synthesis gas for the manufacture of ammonia, alcohols and synthetic liquid fuels. Most of the techniques employed for CO_2 capture in the examples mentioned are also similar to those used in pre-combustion capture. Other industrial process streams which are a source of CO_2 that is not captured, include cement and steel production and fermentation processes for food and drink production. CO_2 could be captured from these streams using techniques that are common to post-combustion capture, oxy-fuel combustion capture and pre-combustion capture (see below and Section 3.2).

3.1.2.2 Post-combustion capture

Capture of CO_2 from flue gases produced by combustion of fossil fuels and biomass in air is referred to as post-combustion capture. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates most of the CO_2. The CO_2 is fed to a storage reservoir and the remaining flue gas is discharged to the atmosphere. A chemical sorbent process as described in section 3.1.3.1 would normally be used for CO_2 separation. Other techniques are also being considered but they are not at such an advanced stage of development.

The main systems of reference for post combustion capture beside industrial applications, are today´s installed capacity of 2261 GWe of oil, coal and natural gas power plants (IEA WEO, 2004) and in particular, 155 GWe of supercritical pulverised coal fired plants (IEA CCC, 2005) and 339 GWe of natural gas combined cycle (NGCC) plants, both representing the types of high efficiency power plant technology where CO_2 capture can be best applied (see sections 3.3 and 3.7).

3.1.2.3 Oxy-fuel combustion capture

In oxy-fuel combustion, nearly pure oxygen is used for combustion instead of air, resulting in a flue gas that is mainly CO_2 and H_2O. If fuel is burnt in pure oxygen, the flame temperature is excessively high, but CO_2 and/or H_2O rich flue gas can be recycled to the combustor to moderate the flame temperature. Oxygen is usually produced by low temperature (cryogenic) air separation and novel techniques to supply oxygen to the fuel, such as membranes and chemical looping cycles are being developed. The power plant systems of reference for oxy-fuel combustion capture systems are the same as those noted above for post-combustion capture systems.

3.1.2.4 Pre-combustion capture

Pre-combustion capture involves reacting a fuel with oxygen or air, and/or steam to give mainly a ‘synthesis gas (syngas)’ or ‘fuel gas’ composed of carbon monoxide and hydrogen. The carbon monoxide is reacted with steam in a catalytic reactor, called a shift converter, to give CO_2 and more hydrogen. CO_2 is then separated, usually by a physical or chemical absorption process, resulting in a hydrogen-rich fuel which can be used in many applications, such as boilers, furnaces, gas turbines, engines and fuel cells. These systems are regarded as having strategic importance (see Section 3.5) but the power plant systems of reference today are 4 GWe of both oil and coal-based, integrated gasification combined cycles (IGCC) which are around 0.1% of total installed capacity word wide (3719 GWe; IEA WEO, 2004). Other reference systems for the application of pre-combustion capture include substantially more capacity than that identified above for IGCC in existing natural gas, oil and coal based syngas/hydrogen production facilities and other types of industrial systems described in more detail in Sections 3.2 and 3.5.

3.1.3 Types of CO_2 capture technologies

CO_2 capture systems use many of the known technologies for gas separation which are integrated into the basic systems for CO_2 capture identified in the last section. A summary of these separation methods is given below while further details are available in standard textbooks.

3.1.3.1 Separation with sorbents

The separation is achieved by putting in intimate contact in a vessel the gas containing the CO_2 with a liquid absorbent or solid sorbent that is capable of capturing the CO_2. In the general scheme of Figure 3.2a the sorbent loaded with the captured CO_2 is transported to a different vessel, where it releases the CO_2 (regeneration) after being heated, after a pressure decrease or after any other change in the conditions around the sorbent. The sorbent resulting after the regeneration step is sent back to capture more CO_2 in a cyclic process. In some variants of this scheme the sorbent is a solid and does not circulate between vessels because the sorption and regeneration are achieved by cyclic changes (in pressure or temperature) in the vessel where the sorbent is contained. A makeup flow of fresh sorbent is always required to compensate for the natural decay of activity and/or sorbent losses. In some situations, the sorbent may be a solid oxide which reacts in a vessel with fossil fuel or biomass producing heat and mainly CO_2 (see Section 3.4.6). The spent sorbent is then circulated to a second vessel where it is re-oxidised in air for reuse with some loss and make up of fresh sorbent.

The general scheme of Figure 3.2a governs many important CO_2 capture systems, including leading commercial options like chemical absorption system and physical absorption and adsorption. Other emerging processes based on new liquid sorbents, or new solid regenerable sorbents are being developed aimed to overcome the limitations of the existing systems. One common problem of these CO_2 capture systems is that the flow of sorbent between the vessels of Figure 3.2a is large because it has to match the huge flow of CO_2 being processed in the power plant. Therefore, equipment sizes and the energy required for sorbent regeneration are large and tend to translate into an important efficiency penalty and added cost. Also, in systems using expensive sorbent materials there is always a danger of escalating cost related to the purchase of the sorbent and the disposal of sorbent residues. Good sorbent performance under high CO_2 loading in many repetitive cycles is obviously a necessary condition in these CO_2 capture systems.

Figure 3.2. General schemes of the main separation processes relevant for CO_2 capture. The gas removed in the separation may be CO_2, H_2 or O_2.

3.1.3.2 Separation with membranes

Membranes are specially manufactured materials that allow the selective permeation of a gas through them. The selectivity of the membrane to different gases is intimately related to the nature of the material, but the flow of gas through the membrane is usually driven by the pressure difference across the membrane. Therefore, high pressure streams are usually preferred for membrane separation. There are many different types of membrane materials (polymeric, metallic, ceramic) that may find application in CO_2 capture systems to preferentially separate H_2 from a fuel gas stream, CO_2 from a range of process streams or O_2 from air with the separated O_2 subsequently aiding the production of a highly concentrated CO_2 stream. Although membrane separation finds many commercial applications in industry today (some of a large scale, like CO_2 separation from natural gas) they have not yet been applied for the large scale and the demanding conditions in terms of reliability and low cost required for CO_2 capture systems. A large R & D effort worldwide is in progress aiming at the manufacture of more suitable membrane materials for CO_2 capture in large scale applications.

3.1.3.3 Distillation of a liquefied gas stream and refrigerated separation

A gas can be made liquid by a series of compression, cooling and expansion steps. Once in liquid form, the components of the gas can be separated in a distillation column. For the case of air, this operation is carried out commercially today on a large scale. Oxygen can be separated from air following the scheme of Figure 3.2c and be used in a range of CO_2 capture systems (oxy-fuel combustion and pre-combustion capture). As in the previous paragraphs the key issue for these systems is the large flow of oxygen required. Refrigerated separation can also be used to separate CO_2 from other gases. It can be used to separate impurities from relatively high purity CO_2 streams, for example from oxy-fuel combustion, and for CO_2 removal from natural gas or synthesis gas that has undergone a shift conversion of CO to CO_2.

3.1.4 Application of CO_2 capture

The CO_2 capture systems shown in Figure 3.1 can be cross-referenced with the different separation technologies of Figure 3.2, resulting in a capture toolbox. Table 3.1 gives an overview of both current and emerging technologies in this toolbox. In the next sections of this chapter a more detailed description of all these technological options will be given, with more emphasis on the most developed technologies for which the CO_2 capture cost can be estimated most reliably. These leading commercial options are shown in bold in Table 3. 1. An overview of the wide range of emerging options being investigated worldwide for CO_2 capture applications will also be provided. All these options are aimed at more efficient and lower cost CO_2 capture systems (compared with the leading options). It is important to understand that this wide variety of approaches for CO_2 capture will tend to settle with time as the expected benefits (and potential weaknesses) in the technological portfolio of Table 3. 1 becomes obvious with new results from current and future research and demonstration projects. Only a few of these options will prove truly cost-effective in the medium to long term.

Table 3.1. Capture toolbox.

CO_2 capture may be installed in new energy utilisation plants or it may be retrofitted to existing plants. In principle, if CO_2 capture is to be introduced rapidly, it may have to be retrofitted to some existing plants or these plants would have to be retired prematurely and replaced by new plants with capture. Disadvantages of retrofits are:

- There may be site constraints such as availability of land for the capture equipment.
- A long remaining plant life may be needed to justify the large expense of installing capture equipment.
- Old plants tend to have low energy efficiencies. Including CO_2 capture will have a proportionally greater impact on the net output than in high efficiency plants.

To minimize the site constraints, new energy utilisation plants could be built “capture-ready”, i.e. with the process design initially factoring in the changes necessary to add capture and with sufficient space and facilities made available for simple installation of CO_2 capture at a later date. For some types of capture retrofit, e.g. pre-combustion capture and oxy-fuel combustion, much of the retrofit equipment could be built on a separate site if necessary.

The other barriers could be largely overcome by upgrading or substantially rebuilding the existing plant when capture is retrofitted. For example, old inefficient boilers and steam turbines could be replaced by modern high efficiency supercritical boilers and turbines or IGCC plants. Because the efficiencies of power generation technologies are increasing, it is possible that the efficiency of the retrofitted plant with CO_2 capture could be as high as that of the original plant without capture.

3.2 Industrial process capture systems

3.2.1 Introduction

There are several applications in industry involving process streams where the opportunity exists to capture CO_2 in large quantities and at costs lower than from the systems described in the rest of this chapter. Capture from these sources will not be the complete answer to the needs of climate change, since the volumes of combustion-generated CO_2 are much higher, but it may well be the place where the first capture and storage occurs.

3.2.2 Natural gas sweetening

Natural gas contains different concentration levels of CO_2, depending on its source, which must be removed. Often pipeline specifications require that the CO_2 concentration be lowered to around 2% by volume (although this amount varies in different places) to prevent pipeline corrosion, to avoid excess energy for transport and to increase the heating value of the gas. Whilst accurate figures are published for annual worldwide natural gas production (BP, 2004), none seem to be published on how much of that gas may contain CO_2. Nevertheless, a reasonable assumption is that about half of raw natural gas production contains CO_2 at concentrations averaging at least 4% by volume. For the purposes of illustration of the scale of this CO_2 capture and storage opportunity, it may be worth using these numbers. So, if half of the worldwide production in 2003 of 2,618.5 billion m^3 of natural gas is reduced in CO_2 content from 4 to 2% mol, the resultant amount of CO_2 removed would be at least 50 million tonnes/year CO_2. It is interesting to note that there are two operating natural gas plants capturing and storing CO_2, BP's In Salah plant in Algeria and a Statoil plant at Sleipner in the North Sea. Both capture about 1 million tonnes CO_2/year (see Chapter 5). About 6.5 million tonnes per year CO_2 from natural gas sweetening is also currently being used in enhanced oil recovery (EOR) in the United States (Beecy and Kuuskraa, 2005) where in these commercial EOR projects, a large fraction of the injected CO_2 is also retained underground (see Chapter 5).

Depending on the level of CO_2 in natural gas, different processes for natural gas sweetening (i.e. H_2S and CO_2 removal) are available (Kohl and Nielsen, 1997 and Maddox and Morgan, 1998):

- Chemical solvents
- Physical solvents
- Membranes.

Natural gas sweetening using various alkanolamines (MEA, DEA, MDEA, etc; See Table 3.2), or a mixture of them, is the most commonly used method. The process flow diagram for CO_2 recovery from natural gas is similar to what is presented for flue gas treatment (see Figure 3.4, Section 3.3.2.1), except that in natural gas processing, absorption occurs at high pressure, with subsequent expansion before the stripper column, where CO_2 will be flashed and separated. When the CO_2 concentration in natural gas is high, membrane systems may be more economical. Industrial application of membranes for recovery of CO_2 from natural gas started in the early 1980's for small units, with many design parameters unknown (Noble and Stern, 1995). It is now a well-established and competitive technology with advantages compared to other technologies, including amine treatment in certain cases (Tabe-Mohammadi, 1999). These advantages include lower capital cost, ease of skid-mounted installation, lower energy consumption, ability to be applied in remote areas, especially offshore and flexibility.

3.2.3 Steel production

The iron and steel industry is the largest energy consuming manufacturing sector in the world, accounting for 10-15% of total industrial energy consumption (IEA GHG, 2000a). Associated CO_2

emissions were estimated at 1,442 million tonnes CO_2 in 1995. Two types of iron and steel making technologies are in operation today. The integrated steel plant has a typical capacity of 3 to 5 million tonnes/year of steel and uses coal as its basic fuel with, in many cases, additional natural gas and oil. The mini-mill uses electric arc furnaces to melt scrap with a typical output of 1 million tonnes/year of steel and an electrical consumption of 300-350 kWh/tonne of steel. Increasingly mini-mills blend direct reduced iron (DRI) with scrap to increase steel quality. The production of direct reduced iron involves reaction of high oxygen content iron ore with H_2 and CO to form reduced iron plus H_2O and CO_2. As a result, many of the direct reduction iron processes could capture a pure CO_2 stream.

An important and growing trend is the use of new iron making processes, which can use lower grade coal than the coking coals required for blast furnace operation. A good example is the COREX process (von Bogdandy, 1989), which produces a large additional quantity of N_2-free fuel gas which can be used in a secondary operation to convert iron ore to iron. Complete CO_2 capture from this process should be possible with this arrangement since the CO_2 and H_2O present in the COREX top gas must be removed to allow the CO plus H_2 to be heated and used to reduce iron oxide to iron in the secondary shaft kiln. This process will produce a combination of molten iron and iron with high recovery of CO_2 derived from the coal feed to the COREX process.

Other opportunities exist for the capture of CO_2 emissions from the iron and steel industry, such as:

- CO_2 recovery from blast furnace gas and recycle of CO-rich top gas to the furnace. A minimum quantity of coke is still required and the blast furnace is fed with a mixture of pure O_2 and recycled top gas. The furnace is, in effect, converted from air firing to oxy-fuel firing with CO_2 capture (see Section 3.4). This would recover 70% of the CO_2 currently emitted from an integrated steel plant (Dongke, Kong and Lu, 1988). It would be feasible to retrofit existing blast furnaces with this process.
- Direct reduction of iron ore, using hydrogen derived from a fossil fuel in a pre-combustion capture step (see Section 3.5) (Duarte and Reich, 1998). Instead of the fuel being burnt in the furnace and releasing its CO_2 to atmosphere, the fuel would be converted to hydrogen and the CO_2 would be captured during that process. The hydrogen would then be used as a reduction agent for the iron ore. Capture rates should be 90-95% according to the design of the pre-combustion capture technique (see Section 3.5).

3.2.4 Cement production

Emissions of CO_2 from the cement industry account for 6% of the total emissions of CO_2 from stationary sources (see Chapter 2). Cement production requires large quantities of fuel to drive the high temperature, energy intensive reactions associated with the calcination of the limestone – that is calcium carbonate being converted to calcium oxide with the evolution of CO_2.

Today, CO_2 is not captured from cement plants, but possibilities do exist. The concentration of CO_2 in the flue gases is between 15-30 % vol, which is higher than in flue gases from power and heat production (2-15% vol). So, in principle, the post-combustion technologies for CO_2 capture described in Section 3.3 could be applied to cement production plants, but would require the additional generation of steam in a cement plant to regenerate the solvent used to capture CO_2. Also, oxy-fuel combustion capture systems may become a promising technique to recover CO_2 (IEA GHG, 1999). Another emerging option would be the use of calcium sorbents for CO_2 capture (see Sections 3.3.3.4 and 3.5.3.5) as Calcium carbonate (limestone) is currently already a raw material used in cement plants. All of these capture techniques could be applied to retrofit, or new plant applications.

3.2.5 Ammonia production

CO_2 is a by-product of ammonia (NH_3) production (Leites, Sama and Lior, 2003). Two main groups of processes are used:

- Steam reforming of light hydrocarbons (natural gas, liquefied petroleum gas, naphtha)
- Partial oxidation or gasification of heavy hydrocarbons (coal, heavy fuel oil, vacuum residue).

Around 85% of world ammonia is made by processes in the steam methane reforming group and so a description of the process is useful. Although the processes vary in detail, they all comprise the following steps:

1. Purification of the feed
2. Primary steam methane reforming (see Section 3.5.2.1)
3. Secondary reforming, with the addition of air, commonly called auto thermal reforming (see Section 3.5.2.3)
4. Shift conversion of CO and H_2O to CO_2 and H_2
5. Removal of CO_2
6. Methanation (a process that reacts and removes trace CO and CO_2)
7. Ammonia synthesis.

Of interest to this report is the removal of CO_2 as a pure stream. A typical modern plant will use the amine solvent process to treat 200,000 Nm^3 /h of gas from the reformer, to produce 72 tonnes/h of concentrated CO_2 (Apple, 1997). The amount of CO_2 produced in modern plants from natural gas is ~1.27 tonnes CO_2/tonne NH_3. Hence, with world ammonia production of about 100 million tonnes/year, one can infer that ~ 127 million tonnes/year of CO_2 is produced. However, it should be noted that this is not all available for storage as, very often, ammonia plants are combined with urea plants, which are capable of utilising 70-90% of the CO_2. About 0.7 million tonnes/year of CO_2 captured from ammonia plants is currently used for enhanced oil recovery in the United States (Beecy and Kuuskraa, 2005) with a large fraction of the injected CO_2 being retained underground (see Chapter 5) in these commercial EOR projects.

3.2.6 Status and outlook

We have reviewed processes – current and potential - that may be used to separate CO_2 in the course of producing another product. One of these processes, natural gas sweetening, is already being used in two industrial plants to capture and store about 2 million tonnes/y of CO_2 for the purposes of climate change mitigation. In the case of ammonia production, pure CO_2 is already being separated. Over 7 million tonnes/year of CO_2 captured from both natural gas sweetening and ammonia plants is currently being used in enhanced oil recovery with some storage (see also Chapter 5) of the injected CO_2 in these commercial EOR projects. Several potential processes for CO_2 capture in steel and cement production exist, but none have yet been applied. Although the total amount of CO_2 that may be captured from these industrial processes is insignificant in terms of the scale of the climate change challenge, significance may arise in that their use could be early exemplars of solutions that can be applied on larger scale elsewhere.

3.3 Post-combustion capture systems

3.3.1 Introduction

Current anthropogenic CO_2 emissions from stationary sources come mostly from combustion systems such as power plants, cement kilns, furnaces in industries, and iron and steel production

plants (see Chapter 2). In these large-scale processes, the direct firing of fuel with air in a combustion chamber has been (for centuries, as it is today) the most economic technology to extract and use the energy contained in the fuel. Therefore, the strategic importance of post-combustion capture systems becomes evident when confronted with the reality of today's sources of CO_2 emissions. Figure 2.1 (Chapter 2) shows that any attempt to mitigate CO_2 emissions from stationary sources on a relevant scale using CO_2 capture and storage, will have to address CO_2 capture from combustion systems. All the CO_2 capture systems described in this section are aimed at the separation of CO_2 from the flue gases generated in a large scale combustion process fired with fossil fuels. Similar capture systems can also be applied to biomass fired combustion processes that tend to be used in much smaller scale compared to those for fossil fuels.

Flue gases or stack gases found in combustion systems usually are at atmospheric pressure. Because of the low pressure, the large presence of nitrogen from air and the large scale of the units, huge flows of gases are generated, the largest example of which may be the stack emissions coming from a natural gas combined cycle power plant having a maximum capacity of around 5 million normal cubic meters per hour. CO_2 contents of flue gases vary depending on the type of fuel used (between 3% for a natural gas combined cycle to less than 15% by volume for a coal fired combustion plant See Table 2.1). In principle post-combustion capture systems can be applied to flue gases produced from the combustion of any type of fuel. However, the impurities in the fuel are very important for the design and costing of the complete plant (Rao and Rubin, 2002). Flue gases coming from coal combustion will contain not only CO_2, N_2, O_2, and H_2O, but also air pollutants such as SO_x, NO_x, particulates, HCl, HF, mercury, other metals, and other trace organic and inorganic contaminants. Figure 3.3 shows a general schematic of a coal fired power plant in which additional unit operations are deployed to remove the air pollutants prior to CO_2 capture in an absorption based process. Although capture of CO_2 in these flue gases is in principle more problematic and energy intensive than from other gas streams, commercial experience is available at a sufficiently large scale (see Section 3.3.2) to provide the basis for cost estimates for post-combustion CO_2 capture systems (see Section 3.7). Also, a large R&D effort is being undertaken worldwide to develop more efficient and lower cost post-combustion systems (see Section 3.3.3), following all possible approaches for the CO_2 separation step (using sorbents, membranes or cryogenics; see Section 3.1.3).

Figure 3.3. Schematic of a pulverised coal-fired power plant with an amine-based CO_2 capture system and other emission controls.

3.3.2 Existing technologies

There are several commercially available process technologies which in principle can be used for CO_2 capture from flue gases. However, comparative assessment studies (Hendriks, 1994; Riemer and Ormerod, 1995; IEA GHG, 2000b) have shown that absorption processes based on chemical solvents are currently the preferred option for post-combustion CO_2 capture. At this point in time, they offer high capture efficiency and selectivity, the lowest energy use and costs when compared with other existing post combustion capture processes. Absorption processes have reached the commercial stage of operation for post-combustion CO_2 capture systems, albeit not on the scale required for power plant flue gases. Therefore, the following paragraphs are devoted to review existing knowledge of the technology and the key technical and environmental issues relevant to the application of this currently leading commercial option for CO_2 capture. The fundamentals of the CO_2 separation step using commercial chemical absorption processes are discussed first. The requirements of flue gas pre-treatment (removal of pollutants other than CO_2) and the energy requirements for regeneration of the chemical solvent follow.

3.3.2.1 Absorption processes

Absorption processes in post-combustion capture make use of the reversible nature of the chemical reaction of an aqueous alkaline solvent, usually an amine, with an acid or sour gas. The process flow diagram of a commercial absorption system is presented in Figure 3.4. After cooling the flue gas, it is brought into contact with the solvent in the absorber. A blower is required to overcome the pressure drop through the absorber. At absorber temperatures typically between 40 and 60 ^{o}C, CO_2 is bound by the chemical solvent in the absorber. The flue gas then undergoes a water wash section to balance water in the system and to remove any solvent droplets or solvent vapour carried over and then leaves the absorber. It is possible to reduce CO_2 concentration in the exit gas down to very low values, as a result of the chemical reaction in the solvent, but with lower exit concentrations tending to increase the height of the absorption vessel. The "rich" solvent, which contains the chemically bound CO_2 is then pumped to the top of a stripper (or regeneration vessel), via a heat exchanger. The regeneration of the chemical solvent is carried out in the stripper at elevated temperatures (100 – 140 ^{o}C) and pressures not very much higher than atmospheric pressure. Heat is supplied to the reboiler to maintain the regeneration conditions. This leads to a thermal energy penalty as a result of heating up the solvent, providing the required de-sorption heat for removing the chemically bound CO_2 and for steam production which acts as a stripping gas. Steam is recovered in the condenser and fed back to the stripper, whereas the CO_2 product gas leaves the stripper. The "lean" solvent, containing far less CO_2 is then pumped back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber temperature level.

Figure 3.4 also shows some additional equipment needed to maintain the solution quality as a result of the formation of degradation products, corrosion products and the presence of particles. This is generally done using filters, carbon beds and a thermally operated reclaimer. Control of degradation and corrosion has in fact been an important aspect in the development of absorption processes over the past few decades.

Figure 3.4. Process flow diagram for CO_2 recovery from flue gas by chemical absorption.

The key parameters determining the technical and economic operation of a CO_2 absorption system are:

- **Flue gas flow rate** -The flue gas flow rate will determine the size of the absorber and the absorber represents a sizeable contribution to the overall cost.
- **CO_2 content in flue gas** - Since flue gas is usually at atmospheric pressure, the partial pressure of CO_2 will be as low as 3 to 14 kPa. Under these low CO_2 partial pressure conditions, aqueous amines (chemical solvents) are most suitable amongst absorption solvents (Kohl and Nielsen, 1997).
- **CO_2 removal** - In practice, typical CO_2 recoveries are between 80% and 95%. The exact recovery choice is an economic trade-off, a higher recovery will lead to a taller absorption column, higher energy penalties and hence increased costs.
- **Solvent flow rate** - The solvent flow rate will determine the size of most equipment apart from the absorber. For a given solvent, the flow rate will be fixed by the previous parameters and also the chosen CO_2 concentrations within the lean and the rich solutions.
- **Energy requirement** - The energy consumption of the process is the sum of the thermal energy needed to regenerate the solvents and the electrical energy required to operate liquid pumps and the flue gas blower or fan. Energy is also required to compress the CO_2 recovered to the final pressure required for transport and storage.

- **Cooling requirement** - Cooling is needed to bring the flue gas and solvent temperatures down to temperature levels required for efficient absorption of CO_2. Also, the product from the stripper will require cooling to recover steam from the stripping process.

The purity and pressure of CO_2 typically recovered from an amine based chemical absorption process are as follows (Sander and Mariz, 1992):

- CO_2 Purity 99.9 vol.% or more (water saturated conditions)
- CO_2 Pressure 50 kPa (gauge)

A further CO_2 purification step makes it possible to bring the CO_2-quality up to food-grade standard. This is required for use in beverages and packaging.

Since combustion flue gases are generally at atmospheric pressure and the CO_2 is diluted, the CO_2 partial pressure is very low. Also, flue gas contains oxygen and other impurities; therefore an important characteristic of an absorption process is in the proper choice of solvent for the given process duty. High CO_2 loading and low heat of desorption energy are essential for atmospheric flue gas CO_2 recovery. The solvents must also have low by-product formation and low decomposition rates, to maintain solvent performance and to limit the amount of waste materials produced. The important effect of other contaminants on the solvent is discussed in Section 3.3.2.2.

The following three absorption processes are commercially available for CO_2 capture in post-combustion systems:

- The Kerr-McGee / ABB Lummus Crest Process (Barchas and Davis, 1992) - This process recovers CO_2 from coke and coal-fired boilers, delivering CO_2 for soda ash and liquid CO_2 preparations. It uses a 15 to 20 wt% aqueous MEA (Mono-Ethanolamine) solution. The largest capacity experienced for this process is 800 tonnes/day of CO_2 utilising two parallel trains (Arnold et.al. 1982).
- The Fluor Daniel ® ECONAMINE ™ Process (Sander and Mariz, 1992, Chapel et. al.,1999) - This process was acquired by Fluor Daniel Inc. from Dow Chemical Company in 1989. It is a MEA based process (30 wt% aqueous solution) with an inhibitor to resist carbon steel corrosion and is specifically tailored for oxygen containing gas streams. It has been used in many plants worldwide recovering up to 320 tonnes/day of CO_2 in a single train for use in beverage and urea production.
- The Kansai Electric Power Co., Mitsubishi Heavy Industries, Ltd., KEPCO/MHI Process (Mimura et al., 1999 and 2003) - The process is based upon sterically hindered amines and already three solvents (KS-1, KS-2 and KS-3) have been developed. KS-1 was commercialised in a urea production application. In this process, low amine losses and low solvent degradation has been noted without the use of inhibitors or additives. As shown in Figure 3.5, the first commercial plant at 200 tonnes/day CO_2 recovery from a flue gas stream has been operating in Malaysia since 1999 for urea production (equivalent to the emissions from a 10 MWt coal-fired power plant)

Figure 3.5. CO_2 capture plant in Malaysia using a 200 tonnes/day KEPCO/MHI chemical solvent process (Courtesy of Mitsubishi).

The performance of the chemical solvent in the operation is maintained by replacement, filtering, and reclaiming, which leads to a consumables requirement. Typical values for the solvent consumption are between 0.2 and 1.6 kg/tonne CO_2. In addition, chemicals are needed to reclaim the amine from the heat stable salt (typically 0.03 – 0.13 kg NaOH/tonne CO_2) and to remove decomposition products (typically

0.03 - 0.06 kg activated carbon/tonne CO_2). The ranges are primarily dependent on the absorption process, with KS-1 being at the low end of the range and ECONAMINE ™ at the high end.

3.3.2.2 Flue Gas Pre-treatment

Flue gases from a combustion power plant are usually above 100°C, which means that they need to cooled down to the temperature levels required for the absorption process. This can be done in a cooler with direct water contact, which also acts as a flue gas wash with additional removal of fine particulates.

In addition to the above, flue gas from coal combustion will contain other acid gas components such as NO_x and SO_x. Flue gases from natural gas combustion will normally only contain NO_x. These acidic gas components will, similar to CO_2, have a chemical interaction with the alkaline solvent. This is not desirable as the irreversible nature of this interaction leads to the formation of heat stable salts and hence a loss in absorption capacity of the solvent and the risk of formation of solids in the solution. It also results in an extra consumption of chemicals to regenerate the solvent and the production of a waste stream such as sodium sulphate or sodium nitrate. Therefore, the pre-removal of NO_x and SO_x to very low values before CO_2 recovery becomes essential. For NO_x it is the NO_2 which leads to the formation of heat stable salts. Fortunately, the level of NO_2 is mostly less than 10% of the overall NO_x content in a flue gas (Chapel et.al. 1999).

The allowable SO_x-content in the flue gas is primarily determined by the cost of the solvent - as this is consumed by reaction with SO_x. SO_2 concentrations in the flue gas are typically around 300 – 5000 ppmv. Commercially available SO_2-removal plants will remove up to 98-99%. Amines are relatively cheap chemicals, but even cheap solvents like MEA (with a price around 1.25 US$/kg (Rao and Rubin, 2002) may require SO_x concentrations of around 10 ppmv, to keep solvent consumption (around 1.6 kg of MEA/tonne of CO_2 separated) and make up costs at reasonable values, which often means that additional flue gas desulphurisation is needed. The optimal SO_2 content, before the CO_2 absorption process is a cost trade-off between CO_2-solvent consumption and SO_2-removal costs. For the Kerr-Mcgee /ABB Lummus Crest Technology, SO_2-removal is typically not justified for SO_2 levels below 50 ppmv (Barchas and Davis, 1992). For the Fluor Daniel Econamine FG process a maximum of 10 ppmv SO_2 content is generally set as the feed gas specification (Sander and Mariz, 1992). This can be met by using alkaline salt solutions in a spray scrubber (Chapel et. al., 1999). A SO_2 scrubber might also double as a direct contact cooler to cool down the flue gas.

Careful attention must also be paid to fly ash and soot present in the flue gas, as they might plug the absorber if contaminants levels are too high. Often the requirements of other flue gas treatment are such that precautions have already been taken. In case of CO_2 recovery from a coal fired boiler flue gas, typically the plant has to be equipped with a $DeNO_x$ unit, an electrostatic precipitator or a bag house filter and a $DeSO_x$ or flue gas desulphurisation unit as part of the environmental protection of the power plant facilities. In some cases, these environmental protection facilities are not enough to carry out deep SO_x removal up to the1~2 ppmv level sometimes needed to minimize solvent consumption and its reclamation from sticking of solvent wastes on reclaimer tube surfaces.

3.3.2.3 Power generation efficiency penalty in CO_2 capture

A key feature of post-combustion CO_2 capture processes based on absorption is the high energy requirement and the resulting efficiency penalty on power cycles. This is primarily due to the heat necessary to regenerate the solvent, steam use for stripping and to a lesser extent the electricity required for liquid pumping, the flue gas fan and finally compression of the CO_2 product. Later in

this chapter, Sections 3.6 and 3.7 present summaries of CO_2 capture energy requirements for a variety of power systems, and discuss the environmental and economic implications of these energy demands.

In principle, the thermal energy for the regeneration process can be supplied by an auxiliary boiler in a retrofit situation. Most studies, however, focus on an overall process in which the absorption process is integrated into the power plant. The heat requirement is at such levels that low pressure steam, e.g. condensing at 0.3 MPa(g), can be used in the reboiler. The steam required for the regeneration process is then extracted from the steam cycle in the power plant. For a coal fired power station, low pressure steam will be extracted prior to the last expansion stage of the steam turbine. For a natural gas fired combined cycle, low pressure steam will be extracted from the last stage in the heat recovery steam generator. Some of this heat can be recovered by preheating the boiler feed water (Hendriks, 1994). Values for the heat requirement for the leading absorption technologies are between 2.7 and 3.3 GJ/tonne CO_2, depending on the solvent process. Typical values for the electricity requirement are between 0.06 and 0.11 GJ/tonne CO_2 for post-combustion capture in coal fired power plants and 0.21 and 0.33 GJ/tonne CO_2 for post-combustion capture in natural gas fired combined cycles. Compression of the CO_2 to 110 bar will require around 0.4 GJ/tonne CO_2 (IEA GHG, 2004).

Integration of the absorption process with an existing power plant will require modifications of the low pressure part of the steam cycle, as a sizeable fraction of the steam will be extracted and hence will not be available to produce power (Nsakala et.al., 2001, Mimura et.al.,1995, Mimura et. al., 1997). To limit the required modifications, small back pressure steam turbines using medium pressure steam to drive the flue gas fan and boiler feed water pumps can be used. The steam is then condensed in the reboiler (Mimura et. al, 1999). Furthermore, in power plants based on steam cycles more than 50% thermal energy in the steam cycle is disposed off in the steam condenser. If the steam cycle system and CO_2 recovery can be integrated, part of the waste heat disposed by the steam condenser can be utilised for regeneration of the chemical solvent.

The reduction of the energy penalty is, nevertheless, closely linked to the chosen solvent system. The IEA Greenhouse Programme (IEA GHG) has carried out performance assessments of power plants with post-combustion capture of CO_2 taking into consideration the most recent improvements in post-combustion CO_2 capture processes identified by technology licensors (IEA GHG, 2004). In this study, Mitsui Babcock Energy Ltd. and Alstom provided information on the use of a high efficiency, ultra-supercritical steam cycle (29 MPa, 600°C, 620° C reheat) boiler and steam turbine for a coal-fired power plant, while for the NGCC case, a combined cycle using a GE 9FA gas turbine was adopted. Fluor provided information on the Fluor Econamine + process based on MEA, and MHI provided information on KEPCO/MHI process based on the KS-1 solvent for CO_2 capture. CO_2 leaving these systems were compressed to a pressure of 11 MPa. The overall net power plant efficiencies with and without CO_2 capture are shown in Figure 3.6, while Figure 3.7 shows the efficiency penalty for CO_2 capture. Overall, results from this study show that the efficiency penalty for post combustion capture in coal and gas fired plant is lower for KEPCO/MHI's CO_2 absorption process. For the purpose of comparison, the performance of power plants with pre-combustion and oxy-fuel capture, based on the same standard set of plant design criteria are also shown in Figures 3.6 and 3.7.

Figure 3.6. Thermal efficiencies of power plants with and without CO_2 capture, % LHV basis (Source data: Davison 2005, IEA GHG 2004, IEA GHG 2003, IEA GHG 2000b, Dillon et.al., 2005).

Figure 3.7. Percentage increase in fuel use per kWh of electricity due to CO_2 capture, compared to the same plant without capture (Source data: Davison 2005, IEA GHG 2004, IEA GHG 2003, IEA GHG 2000b, Dillon *et.al.*, 2005).

3.3.2.4 Effluents

As a result of decomposition of amines, effluents will be created, particularly ammonia and heat-stable salts. Rao and Rubin (2002) have estimated these emissions for an MEA-based process based on limited data. In such processes, heat stable salts (solvent decomposition products, corrosion products etc.) are removed from the solution in a reclaimer and a waste stream is created and is disposed of using normal HSE (Health, Safety and Enviromental) practices. In some cases, these reclaimer bottoms may be classified as a hazardous waste, requiring special handling (Rao and Rubin, 2002). Also a particle filter and carbon filter is normally installed in the solvent circuit to remove by-products. Finally, some solvent material will be lost to the environment through evaporation and carry over in the absorber, which is accounted for in the solvent consumption. It is expected that acid gases other than CO_2, which are still present in the flue gas (SO_x and NO_2) will also be absorbed in the solution. This will lower the concentration of these components further and even the net emissions in some cases depending on the amount of additional energy use for CO_2 capture (see Tables 3.4 and 3.5). As SO_2-removal prior to CO_2-removal is very likely in coal-fired plants, this will lead to the production of a waste or by product stream containing gypsum and water from the FGD unit.

3.3.3 Emerging Technologies

3.3.3.1 Other Absorption Process

Various novel solvents are being investigated, with the object of achieving a reduced energy consumption for solvent regeneration (Chakma, 1995; Chakma and Tontiwachwuthikul, 1999; Mimura et al., 1999; Zheng et al., 2003; Cullinane and Rochelle, 2003; Leites, 1998; Erga et.al, 1995; Aresta and Dibenedetto, 2003; Bai and Yeh, 1997).

Beside novel solvents, novel process designs are also currently becoming available (Leites et. al. 2003). Research is also being carried out to improve upon the existing practices and packing types (Aroonwilas et. al, 2003). Another area of research is to increase of concentration levels of aqueous MEA solution used in absorption systems as this tends to reduce the size of equipment used in capture plants (Aboudheir et.al., 2003). Also methods to prevent oxidative degradation of MEA by de-oxygenation of the solvent solutions are being investigated (Chakravarti et. al., 2001). In addition to this, the catalytic removal of oxygen in flue gases from coal firing has been suggested (Nsakala, et. al. 2001) to enable operation with promising solvents sensitive to oxygen.

3.3.3.2 Adsorption Process

In the adsorption process for flue gas CO_2 recovery, molecular sieves or activated carbons are used in adsorbing CO_2. Desorbing CO_2 is then done by the pressure swing operation (PSA) or temperature swing operation (TSA). Most applications are associated with pressure swing adsorption (Ishibashi et al., 1999 and Yokoyama, 2003). Much less attention has been focused on CO_2 removal via temperature swing adsorption, as this technique is less attractive compared to PSA due to the longer cycle times needed to heat up the bed of solid particles during sorbent regeneration. For bulk separations at large scales, it is also essential to limit the length of the unused bed and therefore opt for faster cycle times.

Adsorption processes have been employed for CO_2 removal from synthesis gas for hydrogen production (see Section 3.5.2.9). It has not yet reached a commercial stage for CO_2 recovery from flue gases. The following main R&D activities have been conducted:

- Study of CO_2 removal from flue gas of a thermal power plant by physical adsorption (Ishibashi et al., 1999)
- Study of CO_2 removal from flue gas of a thermal power plant by a combined system with pressure swing adsorption and a super cold separator (Takamura et al., 1999)
- Pilot tests on the recovery of CO_2 from a coal and oil fired power plant, using pressure temperature swing adsorption (PTSA) and an X-type zeolite as an adsorbent (Yokoyama, 2003)

Pilot test results of coal fired flue gas CO_2 recovery by adsorption processes show that the energy consumption for capture (blowers and vacuum pumps) has improved from the original 708 kWh/tonne CO_2 to 560 kWh/tonne CO_2. An energy consumption of 560 kWh/tonne CO_2 is equivalent to a loss corresponding to 21% of the energy output of the power plant. Recovered CO_2 purity is about 99.0 vol % using two stages of a PSA and PTSA system (Ishibashi et. al., 1999).

It can be concluded that based on mathematical models and data from pilot-scale experimental installations, the design of a full-scale industrial adsorption process might be feasible. A serious drawback of all adsorptive methods is the necessity to treat the gaseous feed before CO_2 separation in an adsorber. Operation at high temperature with other sorbents (see section 3.3.3.4) can circumvent this requirement (Sircar and Golden, 2001). In many cases gases have to be also cooled and dried, which limits the attractiveness of PSA, TSA or ESA (electric swing adsorption) vis-à-vis capture by chemical absorption described in previous sections. The development of a new generation of materials that would efficiently adsorb CO_2 will undoubtedly enhance the competitiveness of adsorptive separation in a flue gas application.

3.3.3.3 Membranes

Membrane processes are used commercially for CO_2 removal from natural gas at high pressure and at high CO_2 concentration (see Section 3.2.2). In flue gases, the low CO_2 partial pressure difference provides a low driving force for gas separation. The removal of carbon dioxide using commercially available polymeric gas separation membranes results in higher energy penalties on the power generation efficiency compared to a standard chemical absorption process (Herzog et. al., 1991, Van der Sluijs et. al., 1992 and Feron, 1994). Also, the maximum percentage of CO_2 removed is lower than for a standard chemical absorption processes. Improvements can be made if more selective membranes become available, such as facilitated membranes, described below.

The membrane option currently receiving the most attention is a hybrid membrane – absorbent (or solvent) system. These systems are being developed for flue gas CO_2 recovery. Membrane/solvent systems employ membranes to provide a very high surface area to volume ratio for mass exchange between a gas stream and a solvent resulting in a very compact system. This results in a membrane contactor system in which the membrane forms a gas permeable barrier between a liquid and a gaseous phase. In general, the membrane does not take part in the separation process. In the case of porous membranes, gaseous components diffuse through the pores and are absorbed by the liquid, in cases of non-porous membranes they dissolve in the membrane and diffuse through the membrane. The contact surface area between gas and liquid phase is maintained by the membrane and is independent of the gas and liquid flow rate. The selectivity of the partition is primarily determined by the absorbent (solvent). Absorption in the liquid phase is determined either by physical partition or by a chemical reaction.

The advantages of membrane/solvent systems are avoidance of operational problems occurring in conventional solvent absorption systems (see Section 3.3.2.1) where gas and liquid flows are in direct contact. Operational problems avoided include foaming, flooding entrainment and channelling, and result in the free choice of the gas and liquid flow rates and a fixed interface for mass transfer in the membrane/solvent system. Furthermore, the use of compact membranes result in smaller equipment sizes with capital cost reductions. The choice of a suitable combination of solvent and membrane material is very important. The material characteristics should be such that the transfer of solvent through the membrane is avoided at operating pressure gradients of typically 50–100 kPa, while the transfer of gas is not hindered. The overall process configuration in terms of unit operations would be very similar to a conventional chemical absorption/desorption process (see Figure 3.4). Membrane/solvent systems can be both used in the absorption as well as in the desorption step. Feron and Jansen (2002) and Falk-Pedersen et al (1999) give examples of suitable membrane/solvent systems.

Research and development efforts have also been reported in the area of facilitated transport membranes. Facilitated transport membranes rely on the formation of complexes or reversible chemical reactions of components present in a gas stream with compounds present in the membrane. These complexes or reaction products are then transported through the membrane. Although solution and diffusion still play a role in the transport mechanism, the essential element is the specific chemical interaction of a gas component with a compound in the membrane, the so-called carrier. Like other pressure driven membrane processes, the driving force for the separation comes from a difference in partial pressure of the component to be transported. An important class of facilitated transport membranes is the so-called supported liquid membrane in which the carrier is dissolved into a liquid which is contained in a membrane. For CO_2 separations, carbonates, amines and molten salt hydrates have been suggested as carriers (Feron, 1992). Porous membranes and ion-exchange membranes have been employed as the support. Until now, supported liquid membranes have only been studied on a laboratory scale. Practical problems associated with supported liquid membranes are membrane stability and liquid volatility. Furthermore, the selectivity for a gas decreases with increasing partial pressure on the feed side. This is a result of saturation of the carrier in the liquid. Also, as the total feed pressure is increased, the permeation of unwanted components is increased. This also results in a decrease in selectivity. Finally, selectivity is also reduced by a reduction in membrane thickness. Recent development work has focused on the following technological options that are applicable to both CO_2/N_2 and CO_2/H_2 separations:

- Amine containing membranes (Teramoto et. al., 1996)
- Potassium carbonate containing polymer gel membranes (Okabe et. al., 2003)
- Potassium carbonate-glycerol containing membranes (Chen et. al., 1999)
- Dendrimer containing membranes (Kovvali and Sirkar, 2001)
- Poly-electrolyte membranes (Quinn and Laciak, 1997)

Facilitated transport membranes and other membranes can also be used in a pre-concentration step prior to the liquefaction of CO_2 (Mano, 2002).

3.3.3.4 *Solid Sorbents*

There are post-combustion systems being proposed that make use of regenerable solid sorbents to remove CO_2 at relatively high temperatures. The use of high temperatures in the CO_2 separation step has the potential to reduce efficiency penalties with respect to wet-absorption methods. In principle, they all follow the scheme shown in Figure 3.2a, where the combustion flue gas is put in contact with the sorbent in a suitable reactor to allow the gas-solid reaction of CO_2 with the sorbent (usually the carbonation of a metal oxide). The solid can be easily separated from the gas stream and sent for regeneration in a different reactor. Instead of moving the solids, the reactor can also be

switched between sorption and regeneration modes of operation in a batch wise, cyclic operation. One key component for the development of these systems is obviously the sorbent itself, that has to have good CO_2 absorption capacity and chemical and mechanical stability for long periods of operation in repeated cycles. In general, sorbent performance and cost are critical issues in all post-combustion systems, and more elaborate sorbent materials are usually more expensive and will have to prove outstanding performance compared with existing commercial alternatives such as those described in 3.3.2.

Solid sorbents being investigated for large scale CO_2 capture purposes are sodium and potassium oxides and carbonates (to produce bicarbonate), usually supported on a solid substrate (Hoffman et al, 2002; Green et al, 2002). Also, high temperature Li-based and CaO-based sorbents are suitable candidates. The use of lithium containing compounds (lithium, lithium-zirconia and lithium-silica oxides) in a carbonation-calcination cycle, was first investigated in Japan (Nakagawa et al.,1998). The reported performance of these sorbents is very good, with very high reactivity in a wide range of temperatures below 700ºC, rapid regeneration at higher temperatures and durability in repeated capture-regeneration cycles. This is essential because lithium is an intrinsically expensive material.

The use of CaO as a regenerable CO_2 sorbent has been proposed in several processes dating back to the XIX century. The carbonation reaction of CaO to separate CO_2 from hot gases (T>600ºC) is very fast and the regeneration of the sorbent by calcining the $CaCO_3$ into CaO and pure CO_2 is favoured at T>900ºC (at a partial pressure of CO_2 of 0.1 MPa). The basic separation principle using this carbonation-calcination cycle was successfully tested in a pilot plant (40 t/day) for the development of the Acceptor Coal Gasification Process (Curran, 1967) using two interconnected fluidised beds. The use of the above cycle for a post-combustion system was first proposed by Shimizu et al. (1999) and involved the regeneration of the sorbent in a fluidised bed, firing part of the fuel with O_2 /CO_2 mixtures (see also Section 3.4.2). The effective capture of CO_2 by CaO has been demonstrated in a small pilot fluidised bed (Abanades et al, 2004a). Other combustion cycles incorporating capture of CO_2 with CaO that might not need O_2 are being developed, including one that works at high pressures with simultaneous capture of the CO_2 and SO_2 (Wang et al, 2004). One weak point in all these processes is that natural sorbents (limestones and dolomites) deactivate rapidly, and a large make up flow of sorbent (of the order of the mass flow of fuel entering the plant) is required to maintain the activity in the capture-regeneration loop (Abanades et al, 2004b). Although the deactivated sorbent may find application in the cement industry and the sorbent cost is low, a range of methods to enhance the activity of Ca-based CO_2 sorbents are being pursued by several groups around the world.

3.3.4 Status and outlook

Virtually all the energy we use today from carbon-containing fuels is obtained by directly burning fuels in air. This is despite many decades of exploring promising and more efficient alternative energy conversion cycles that rely on other fuel processing steps prior to fuel combustion or avoiding direct fuel combustion (see pre-combustion capture – Section 3.5). In particular, combustion based systems are still the competitive choice for operators aiming at large scale production of electricity and heat from fossil fuels, even under more demanding environmental regulations, because these processes are reliable and well proven in delivering electricity and heat at prices that often set a bench mark for these services. In addition, there is a continued effort to raise the energy conversion efficiencies of these systems through advanced materials and component development. This will allow these systems to operate at higher temperature and higher efficiency.

As was noted in Section 3.1, the main systems of reference for post combustion capture are today´s installed capacity of coal and natural gas power plants, with a total of 970 GWe sub-critical steam

and 155 GWe of supercritical/ultra supercritical steam based pulverised coal fired plants, 339 GWe of natural gas combined cycle, 333 GWe natural gas steam-electric power plants and 17 GWe of coal-fired circulating fluidised bed combustion (CFBC) power plants. An additional capacity of 454 GWe of oil based power plant, with a significant proportion of these operating in an air firing mode is also noted (IEA WEO, 2004 and IEA CCC, 2005). Current projections indicate that the generation efficiency of commercial pulverised coal fired power plants based on ultra-supercritical steam cycles would exceed 50 % (LHV) over the next decade (IEA, 2004), which will be higher than efficiencies of between 36 and 45 % reported for current sub-critical and supercritical steam based plants without capture (see section 3.7). Similarly, natural gas fired combined cycles are expected to have efficiencies of 65 % by 2020 (IEA GHG, 2002b) and up from current efficiencies between 55 and 58%, see section 3.7). In a future carbon constrained world, these independent and ongoing developments in power cycle efficiencies will result in lower CO_2-emissions per kWh produced and hence a lower loss in overall cycle efficiency when post-combustion capture is applied.

There are proven post-combustion CO_2 capture technologies based on absorption processes that are currently commercially available. They produce CO_2 from flue gases in coal and gas fired installations for food/beverage applications and chemicals production in capacity ranges between 6 and 800 tonnes of CO_2 per day. They require scale up to 20-50 times that of current unit capacities for deployment in large scale power plants in the 500 MW_e capacity range (see section 3.3.2). The inherent limitations of currently available absorption technologies when applied to post-combustion capture systems are well known and their impact on system cost can be estimated relatively accurately for a given application (see section 3.7). Hence, with the dominant role played by air blown energy conversion processes in the global energy infrastructure, the availability of post-combustion capture systems is important if CO_2 capture and storage becomes a viable climate change mitigation strategy.

The intense development efforts on novel solvents for improved performance and reduced energy consumption during regeneration, as well as process designs incorporating new contacting devices such as hybrid membrane-absorbent systems, solid adsorbents, and high temperature regenerable sorbents, may lead to the use of more energy efficient post-combustion capture systems. However, all these novel concepts still need to prove their lower costs and reliability of operation on a commercial scale. The same considerations also apply to other advanced CO_2 capture concepts with oxy-fuel combustion or pre-combustion capture reviewed in the following sections of this chapter. It is generally not yet clear which of these emerging technologies, if any, will succeed as the dominant commercial technology for energy systems incorporating CO_2 capture.

3.4 Oxy-fuel Combustion Capture Systems

3.4.1 Introduction

The oxy-fuel combustion process eliminates nitrogen from the flue gas by combusting a hydrocarbon or carbonaceous fuel in either pure oxygen or a mixture of pure oxygen and a CO_2 rich recycled flue gas (carbonaceous fuels include biomass). Combustion of a fuel with pure oxygen has a combustion temperature of about 3500°C which is far too high for typical power plant materials. The combustion temperature is limited to about 1300-1400°C in a typical gas turbine cycle and to about 1900°C in an oxy-fuel coal fired boiler using current technology. The combustion temperature is controlled by the proportion of flue gas and gaseous or liquid water recycled back to the combustion chamber.

The combustion products (or flue gas) consist mainly of carbon dioxide and water vapour together with excess oxygen required to ensure complete combustion of the fuel. It will also contain any other components in the fuel, any diluents in the oxygen stream supplied, any inerts in the fuel and from air leakage into the system from the atmosphere. The net flue gas, after cooling to condense water vapour, contains from about 80% to 98% CO_2 depending on the fuel used and the particular oxy-fuel combustion process. This concentrated CO_2 stream can be compressed, dried and further purified before delivery into a pipeline for storage (see Chapter 4). The CO_2 capture efficiency is very close to 100% in oxy-fuel combustion capture systems. Impurities in the CO_2 are gas components such as SO_x, NO_x, HCl and Hg derived from the fuel used , and the inert gas components, such as nitrogen, argon and oxygen, derived from the oxygen feed or air leakage into the system. The CO_2 is transported by pipeline as a dense supercritical phase. Inert gases must be reduced to a low concentration to avoid two phase flow conditions developing in the pipeline systems. The acid gas components may need to be removed to comply with legislation covering co-disposal of toxic or hazardous waste or to avoid operations or environmental problems with disposal in deep saline reservoirs, hydrocarbon formations or in the ocean. The carbon dioxide must also be dried to prevent water condensation and corrosion in pipelines and allow use of conventional carbon-steel materials.

Although elements of oxy-fuel combustion technologies are in use in the aluminium, iron and steel and glass melting industries today, oxy-fuel technologies for CO_2 capture have yet to be deployed on a commercial scale. Therefore, the first classification between *existing technologies* and *emerging technologies* adopted in post-combustion (Section 3.3) and pre-combustion (Section 3.5) is not followed in this section. However, it is important to emphasize that the key separation step in most oxy-fuel capture systems (O_2 from air) is an "existing technology" (see Section 3.4.5). Current methods of oxygen production by air separation comprise cryogenic distillation, adsorption using multi-bed pressure swing units and polymeric membranes. For oxy-fuel conversions requiring less than 200 tonne O_2/day, the adsorption system will be economic. For all the larger applications, which include power station boilers, cryogenic air separation is the economic solution (Wilkinson et al., 2003a).

In the following sections we present the main oxy-fuel combustion systems classified according to how the heat of combustion is supplied and whether the flue gas is used as a working fluid (Sections 3.4.2, 3.4.3, 3.4.4). A brief overview of O_2 production methods relevant for these systems is given (Section 3.4.5). In Section 3.4.6, the emerging technology of chemical looping combustion is presented, in which pure oxygen is supplied by a metal oxide rather than an oxygen production process. The section on oxy-fuel systems closes with an overview of the status of the technology (Section 3.4.7).

3.4.2 Oxy-fuel indirect heating - steam cycle

In these systems, the oxy-fuel combustion chamber provides heat to a separate fluid by heat transfer through a surface. It can be used for either process heating, or in a boiler with a steam cycle for power generation. The indirect system can be used with any hydrocarbon or carbon containing fuel.

The application of oxy-fuel indirect heating for CO_2 capture in process heating and power generation has been examined in both pilot-scale trials evaluating the combustion of carbonaceous fuels in oxygen and CO_2 rich recycled flue gas mixtures, and engineering assessments of plant conversions as described below.

3.4.2.1 Oxy-fuel combustion trials

Work to demonstrate the application of oxy-fuel recycle combustion in process heating and for steam generation for use in steam power cycles have been mostly undertaken in pilot scale tests that have looked at the combustion, heat transfer and pollutant forming behaviour of natural gas and coal.

A study was carried out (Babcock Energy Ltd et al., 1995) which included an oxy-fuel test with flue gas recycle using a 160kW, pulverised coal, low NO_x burner. The system included a heat transfer test section to simulate fouling conditions. Test conditions included variation in recycle flow and excess O_2 levels. Measurements included all gas compositions, ash analysis and tube fouling after a five week test run. The work also included a case study on oxy-fuel operation of a 660MW power boiler with CO_2 capture, compression and purification. The main test results were that NO_x levels reduced with increase in recycle rate, while SO_2 and carbon in ash levels were insensitive to the recycle rate. Fouling in the convective test section was greater with oxy-fuel firing than with air. High slagging UK coal had worse slagging when using oxy-fuel firing, the higher excess O_2 level lowered carbon in ash and CO concentration.

For the combustion of pulverised coal, other pilot-scale tests by Croiset and Thambimuthu (2000) have reported that the flame temperature and heat capacity of gases to match fuel burning in air occurs when the feed gas used in oxy-fuel combustion has a composition of approximately 35 vol % O_2 and 65 vol% of dry recycled CO_2 (c.f. 21vol% O_2 and the rest nitrogen in air). In practice, the presence of inerts such as ash and inorganic components in the coal, the specific fuel composition and moisture in the recycled gas stream and the coal feed will result in minor adjustments to this feed mixture composition to keep the flame temperature at a value similar to fuel combustion in air.

At conditions that match O_2/CO_2 recycle combustion to fuel burning in air, coal burning is reported complete (Croiset and Thambimuthu, 2000), with operation of the process at excess O_2 levels in the flue gas as low as 1 - 3 vol% O_2, producing a flue gas stream of 95-98 vol % dry CO_2 (the rest being excess O_2, NO_x, SO_x and Argon) when a very high purity O_2 stream is used in the combustion process with zero leakage of ambient air into the system. No differences were detected in the fly ash formation behaviour in the combustor or SO_2 emissions compared to conventional air firing conditions. For NO_x on the other hand, emissions were lower due to zero thermal NO_x formation from the absence of nitrogen in the feed gas - with the partial recycling of NO_x also reducing the formation and net emissions originating from the fuel bound nitrogen. Other studies have demonstrated that the level of NO_x reduction is as high as 75% compared to coal burning in air (Chatel-Pelage et al., 2003). Similar data for natural gas burning in O_2/CO_2 recycle mixtures report zero thermal NO_x emissions in the absence of air leakage into the boiler, with trace amounts produced as thermal NO_x when residual nitrogen is present in the natural gas feed (Tan et al., 2002).

The above and other findings show that with the application of oxy-fuel combustion in modified utility boilers, the nitrogen-free combustion process would benefit from higher heat transfer rates (McDonald and Palkes, 1999), and if also constructed with higher temperature tolerant materials, are able to operate at higher oxygen concentration and lower flue gas recycle flows – both of which will considerably reduce overall volume flows and size of the boiler.

It should be noted that even when deploying a 2/3 flue gas recycle gas ratio to maintain a 35 vol % O_2 feed to a pulverised coal fired boiler, hot recycling of the flue gas prior to CO_2 purification and compression also reduces the size of all unit operations in the stream leaving the boiler to 1/5 that of similar equipment deployed in conventional air blown combustion systems (Chatel-Pelage et al., 2003). Use of a low temperature gas purification step prior to CO_2 compression (see Section 3.4.2.2)

will also eliminate the need to deploy conventional selective catalytic reduction for NO_x removal and flue gas desulphurization to purify the gas, a practice typically adopted in conventional air blown combustion processes (see Figure 3.3). The overall reduction in flow volumes, equipment scale and simplification of gas purification steps will thus have the benefit of reducing both capital and operating costs of equipment deployed for combustion, heat transfer and final gas purification in process and power plant applications (Marin et al., 2003).

As noted above for pulverised coal, oil, natural gas and biomass combustion, fluidised beds could also be fired with O_2 instead of air to supply heat for the steam cycle. The intense solid mixing in a fluidised bed combustion system can provide very good temperature control even in highly exothermic conditions, thereby minimizing the need for flue gas recycling. In principle, a variety of commercial designs for fluidised combustion boilers exist that could be retrofitted for oxygen firing. A circulating fluidised bed combustor with O_2 firing was proposed by Shimizu et al. (1999) to generate the heat required for the calcination of $CaCO_3$ (see also Section 3.3.3.4). More recently, plans for pilot testing of an oxy-fired circulating fluidised bed boiler have been published by Nsakala et al. (2003).

3.4.2.2 Assessments of Plants converted to oxy-fuel combustion

We discuss here performance data from a recent comprehensive design study for an application of oxy-fuel combustion in a new build pulverised coal fired power boiler using a supercritical steam cycle (see Figure 3.8; Dillon et al., 2004). The overall thermal efficiency on a lower heating value basis is reduced from 44.2% to 35.4%. The net power output is reduced from 677 MW_e to 532 MW_e.

Figure 3.8. Schematic of an Oxy-fuel Pulverised Coal-Fired Power Plant.

Important features of the system include:

- Burner design and gas recycle flow rate have been selected to achieve the same temperatures as in air combustion (compatible temperatures with existing materials in the boiler).
- The CO_2-rich flue gas from the boiler is divided into three gas streams: one to be recycled back to the combustor, one to be used as transport and drying gas of the coal feed and the third as product gas. The first recycle and the product stream are cooled by direct water scrubbing to remove residual particulates, water vapour and soluble acid gases such as SO_3 and HCl. Oxygen and entrained coal dust together with the second recycle stream flow to the burners.
- The air leakage into the boiler is sufficient to give a high enough inerts level to require a low temperature inert gas removal unit to be installed, even if pure O_2 were used as the oxidant in the boiler. The cryogenic oxygen plant will, in this case, produce 95% O_2 purity to minimize power consumption and capital cost.
- The low temperature (-55°C) CO_2 purification plant (Wilkinson et al., 2003b) integrated with the CO_2 compressor will not only remove excess O_2, N_2, argon but can also remove all NO_x and SO_2 from the CO_2 stream, if high purity CO_2 is required for storage. Significantly, removal of these components before final CO_2 compression eliminates the need to otherwise incorporate upstream NO_x and SO_x removal equipment in the net flue gas stream leaving the boiler. Elimination of N_2 from the flue gas results in higher SO_x concentrations in the boiler and reduced NO_x levels. Suitable corrosion resistant materials of construction must be chosen.
- The overall heat transfer is improved in oxy-fuel firing because of the higher emissivity of the CO_2/H_2O gas mixture in the boiler compared to nitrogen and the improved heat transfer in the convection section. These improvements, together with the recycle of hot flue gas, increase the boiler efficiency and steam generation by about 5%-points.

- The overall thermal efficiency is improved by running the O_2 plant air compressor and the first and final stages of the CO_2 compressor without cooling, and recovering the compression heat for boiler feed water heating prior to de-aeration.

Engineering studies have also been reported by Simbeck and McDonald (2001a) and by McDonald and Palkes (1999). This work has confirmed that the concept of retrofitting oxy-fuel combustion with CO_2 capture to existing coal fired power stations does not have any technical barriers and can make use of existing technology systems.

It has been reported (Wilkinson et al., 2003b) that the application of oxy-fuel technology for the retrofit of power plant boilers and a range of refinery heaters in a refinery complex (Grangemouth refinery in Scotland) is technically feasible at a competitive cost compared to other types of CO_2 capture technologies. In this case, the existing boiler is adapted to allow combustion of refinery gas and fuel oil with highly enriched oxygen and with partial flue gas recycling for temperature control. Oxy-fuel boiler conversions only needed minor burner modifications, a new O_2 injection system and controls, and a new flue gas recycle line with a separate blower. These are cheap and relatively simple modifications and result in an increase in boiler/heater thermal efficiency due to the recycle of hot gas. Modifications to a coal fired boiler are more complex. In this study, it was found to be more economic to design the air separation units for only 95% O_2 purity instead of 99.5% to comply with practical levels of air leakage into boilers and to separate the associated argon and nitrogen in the CO_2 inert gas removal system to produce a purity of CO_2 suitable for geological storage. After conversion of the boiler, the CO_2 concentration in the flue gas increases from 17% to 60% while the water content increases from 10 to 30%. Impurities (SO_x, NO_x) and gases (excess O_2, N_2, Argon) representing about 10% of the stream are separated from CO_2 at low temperature (-55°C). After cooling, compression and drying of the separated or non-recycled flue gas, the product for sequestration comprises 96% CO_2 contaminated with 2% N_2, 1% Argon and less than 1% O_2 and SO_2. Production of ultra-pure CO_2 for storage would also be possible by adding distillation steps to the separation process.

3.4.2.3 Advanced Zero Emission Power plant

The Advanced Zero Emission Power plant (Griffin et al., 2003) is an indirect heating gas turbine cycle that incorporates a high-temperature oxygen transport membrane, operating at about 800-1000°C (see Section 3.4.5.2). This process uses a standard air based gas turbine in a combined cycle arrangement. Three process steps take place in a reactor system that replaces the combustion chamber of a standard gas turbine: 1) separation of oxygen from hot air using the membrane and transport to the combustion section; 2) combustion and 3) heat exchange from the combustion products to the compressed air.

A net efficiency for Advanced Zero Emission Power cycle of around 49 – 50 % LHV is claimed including CO_2 compression for transport. In order to get full advantage of the potential of the most advanced gas turbines, which have inlet temperatures of 1300-1400°C, an afterburner fired with natural gas in air may be added behind the reactor system. The efficiency then climbs up to 52% but now 15% of the CO_2 generated by combustion is released at the stack and is not captured.

Figure 3.9. Principle flow scheme of the Advanced Zero Emission Power plant cycle.

3.4.3 Oxy-fuel direct heating - gas turbine cycle

Oxy-fuel combustion takes place in a pressurised CO_2 rich recirculating stream in a modified gas turbine. The hot gas is expanded in the turbine producing power. The turbine exhaust is cooled to

provide heat for a steam cycle and water vapour is condensed by further cooling. The CO_2 rich gas is compressed in the compressor section. The net CO_2 rich combustion product is removed from the system. Only natural gas, light hydrocarbons and syngas ($CO+H_2$) can be used as fuel.

3.4.3.1 Cycle Description and Performance

Figure 3.10 shows how a gas turbine can be adapted to run with oxy-fuel firing using CO_2 as a working fluid. Exhaust gas leaving the heat recovery steam generator is cooled to condense water. The net CO_2 product is removed and the remaining gas is recycled to the compressor- Suitable fuels are natural gas, light to medium hydrocarbons or (H_2 + CO) syngas, which could be derived from coal. The use of CO_2 as the working fluid in the turbine will necessitate a complete redesign of the gas turbine (see Section 3.4.3.2). A recent study (Dillon et al., 2004) gives an overall efficiency including CO_2 compression of 45%.

Figure 3.10. Principle of the oxy-fuel gas turbine combined cycle. Exhaust gas is recycled, compressed and used in the combustion chamber to control the temperature entering the turbine.

Two typical variants of this configuration are the so-called Matiant and Graz cycles (Mathieu, 2003; Jericha et al., 2003). The Matiant cycle uses CO_2 as the working fluid, and consists of features like intercooled compressor and turbine reheat. The exhaust gas is preheating the recycled CO_2 in a heat exchanger. The CO_2 generated in combustion is extracted from the cycle behind the compressor. The net overall LHV efficiency is expected to be 45 to 47% and can increase above 50% in a combined cycle configuration similar to that shown in Figure 3.10. The Graz cycle consists of an integrated gas turbine and steam turbine cycle. A net LHV efficiency of above 50% has been calculated for this cycle (Jericha et al., 2003).

A recent comprehensive review of gas turbine cycles with CO_2 capture provides efficiencies of different cycles on a common basis (Kvamsdal et al., 2004).

3.4.3.2 The CO_2/Oxy-fuel Gas Turbine

In existing gas turbines the molecular weight of the gases in the compressor and turbine are close to that of air (28.8). In the case of oxy-fuel combustion with CO_2-recycle the compressor fluid molecular weight is about 43 and about 40 in the turbine. The change in working fluid from air to a CO_2 rich gas results in a number of changes in properties that are of importance for the design of the compressor, combustor and the hot gas path including the turbine:

- The speed of sound is 80% of air.
- The gas density is 50% higher than air.
- The specific heat ratio is lower than air resulting in a lower temperature change on adiabatic compression or expansion. An oxy-fuel gas turbine in a combined cycle has a higher optimal pressure ratio, typically 30 to 35 compared to 15 to 18 used with air in a combined cycle system. With the highest turbine inlet temperature consistent with material limitations, the rather high pressure ratio results in an exhaust gas temperature of about 600°C, which is optimal for the steam cycle.

These changes in the fundamental properties of the working fluid will have a significant impact on gas turbine components, requiring completely new designs of compressors, combustors (to account for aerodynamic changes and acoustic feedbacks) and hot gas path (O_2 partial pressure must be low in oxy-fuel systems but it is also important to avoid reducing conditions for the materials of the turbine or the change to materials allowing much lower O_2 partial pressures).

3.4.4 Oxy-fuel direct heating - steam turbine cycle

In an oxy-fuel steam turbine cycle, water is pressurised as a liquid and is then evaporated, heated by the direct injection and combustion of a fuel with pure oxygen and expanded in a turbine. Most of the water in the low pressure turbine exhaust gas is cooled and condensed, prior to pumping back to a high pressure while the CO_2 produced from combustion is removed and compressed for pipeline transport. A variant of this cycle in which the heat is provided by burning natural gas fuel in-situ with pure oxygen was proposed by Yantovskii et al. (1992).

The direct combustion of fuel and oxygen has been practised for many years in the metallurgical and glass industries where burners operate at near stoichiometric conditions with flame temperatures of up to 3500°C. A water quenched H_2/O_2 burner capable of producing 60 tonne/h, 6 MPa super heated steam was demonstrated in the mid 1980's (Ramsaier et al., 1985). A recent development by Clean Energy Systems incorporating these concepts where a mixture of 90vol % superheated steam and 10% CO_2 is produced at high temperature and pressure to power conventional or advanced steam turbines is shown in Figure 3.11. The steam is condensed in a low pressure condenser and recycled, while CO_2 is extracted from the condenser, purified and compressed. (Anderson et al., 2003 and Marin et al., 2003).

Figure 3.11. Principle of the Clean Energy Systems cycle. The combustion of the fuel and oxygen is cooled by injection of liquid water, which is recycled in the process.

Plants of this type require a clean gaseous or liquid fuel and will operate at 20 to 50 MPa pressure. The steam plus CO_2 generator is very compact. Control systems must be very precise as start-up and increase to full flow in a preheated plant can take place in less than 2 seconds. Precise control of this very rapid start was demonstrated (Ramsaier et al., 1985) in a 60 tonne steam/h unit. The Clean Energy Systems studies claim efficiencies as high as 55% with CO_2 capture depending on the process conditions used.

The Clean Energy Systems technology can be initially applied with today's steam turbines (565°C inlet temperature). The main technical issue is clearly the design of the steam turbines which could be used at inlet temperatures up to 1300°C by applying technology similar to that used in the hot path of gas turbines. The combustor itself (the "gas generator") is adapted from existing rocket engine technology. In 2000, Clean Energy Systems proved the concept with a 110 kW pilot project conducted at the University of California Davis. A 20 MW thermal gas generator was successfully operated in a test run of the order of a few minutes in early 2003. A zero emissions demonstration plant (up to 6 MW electrical) is now on-line. US Department of Energy's National Energy Technology Laboratory designed the reheater (Richards, 2003) and NASA tested it in 2002. Much more technology development and demonstration is needed on this proposed power cycle, but it shows significant potential for low capital cost and high efficiency.

3.4.5 Techniques and improvements in oxygen production

Oxygen is the key requirement for any oxy-fuel combustion system. It is also a key technology for pre-combustion CO_2 capture (see Section 3.5). In the next paragraphs, existing large scale O_2 production methods are described first, followed by emerging concepts aimed at reducing the energy consumption and cost.

3.4.5.1 Cryogenic Oxygen Production

The very large quantities of oxygen required for CO_2 capture using the techniques of oxy-fuel combustion and pre-combustion de-carbonisation can only be economically produced, at present,

by using the established process of oxygen separation from air by distillation at cryogenic temperatures (Latimer, 1967). This is a technology that has been practiced for over 100 years.

In a typical cryogenic air separation plant (Castle, 1991; Figure 3.12), air is compressed to a pressure of 0.5 to 0.6 MPa, and purified to remove water, CO_2, N_2O and trace hydrocarbons which could accumulate to dangerous levels in oxygen rich parts of the plant such as the reboiler condenser. Two or more switching fixed bed adsorbers are used, which can be regenerated by either temperature or pressure swing, using in each case, a low pressure waste nitrogen stream. The air is cooled against returning products (oxygen and nitrogen) in a battery of aluminium plate-fin heat exchangers and separated into pure oxygen and nitrogen fractions in a double distillation column, which uses aluminium packing.

Figure 3.12. Oxygen production by distillation of liquid air. The illustration shows a 3000 tonne/day oxygen plant (courtesy of Air Products).

Oxygen can be pumped as liquid and delivered as a high pressure gas at up to 10 MPa. Pumped oxygen plants have largely replaced the oxygen gas compression systems. They have virtually identical power consumptions but in a pumped cycle a high pressure air booster compressor provides a means of efficiently vaporising and heating the liquid oxygen stream to ambient temperature. Current plant sizes range up to 3500 tonne O_2/day and larger single train plants are being designed. Typical power consumption for the delivery of 95% O_2 at low pressure (0.17 MPa, a typical pressure for an oxy-fuel application) is 200 to 240 kWh/tonne O_2. There are numerous process cycle variations particularly for the production of oxygen at less than 97.5% purity which have been developed to reduce power and capital cost. Note that adsorption and polymeric membrane methods of air separation are only economic for small oxygen production rates.

3.4.5.2 High Temperature Oxygen Ion Transport Membranes

Ceramic mixed metal oxides have been developed which exhibit simultaneous oxygen ion and electron conduction at temperatures above 500°C and preferably above 700°C (Skinner and Kilner 2003; Boumeester and Van Laar, 2002; Dyer et al., 2000; Bredesen et al., 2004). Typical crystal structures which exhibit these properties include the perovskites and the brownmillerites. The selectivity of these materials for oxygen is infinite. The oxygen permeability is primarily controlled by the oxygen ion vacancies in the metal oxide lattice. A difference in oxygen partial pressure across the membrane will cause oxygen molecules to ionise on the ceramic surface and pass into the crystal structure while simultaneously on the permeate side of the membrane, the oxygen ions give up their electrons and leave the ceramic in the region of lower activity. The electron conduction path is through the metal ions in the lattice. Unlike conventional membranes, the flux through the ceramic is a function of the partial pressure ratio. In the technical literature, the engineered structures of these ceramic mixed metal oxides are referred to as *ion transport membranes, ITM* or *oxygen transport membranes, OTM*.

The oxygen transport membrane can be fabricated in the form of plain tubes or as hollow fins on a central collector tube (Armstrong et al., 2002). The finned elements are then mounted in tube sheets within a pressure vessel with high pressure air flowing over the fins. There are several new concepts that have been proposed for using oxygen transport membranes in power cycles with CO_2 capture. A prime example of an oxy-fuel gas turbine cycle that incorporates an oxygen transport membrane for oxygen production is the Advanced Zero Emission Power plant described in Section 3.4.2.3. Another example is found in Sundnes (1998).

3.4.5.2.1 Development Status

Oxygen transport membrane systems for oxygen production are currently in the early stages of development by at least 2 consortia receiving research funding from the US Department of Energy and the European Commission. The concept has now reached the pilot plant stage and projected cost, manufacturing procedures and performance targets for full size systems have been evaluated. Systems capable of large scale production are projected to be available after industrial demonstration in about 7 years (Armstrong et al., 2002).

3.4.6 Chemical looping combustion

Originally proposed by Richter and Knoche (1983) and with subsequent significant contributions by Ishida and Jin (1994), the main idea of Chemical Looping Combustion is to split combustion of a hydrocarbon or carbonaceous fuel into separate oxidation and reduction reactions by introducing a suitable metal oxide as an oxygen carrier to circulate between two reactors (Figure 3.13). Separation of oxygen from air is accomplished by fixing the oxygen as a metal oxide. No air separation plant is required. The reaction between fuel and oxygen is accomplished in a second reactor by the release of oxygen from the metal oxide in a reducing atmosphere caused by the presence of a hydrocarbon or carbonaceous fuel. The recycle rate of the solid material between the two reactors and the average solids residence time in each reactor, control the heat balance and the temperature levels in each reactor. The effect of having combustion in two reactors compared to conventional combustion in a single stage is that the CO_2 is not diluted with nitrogen gas, but is almost pure after separation from water, without requiring any extra energy demand and costly external equipment for CO_2 separation.

Figure 3.13. The Chemical Looping Combustion principle - in a gas turbine cycle.

Possible metal oxides are some oxides of common transition-state metals, such as iron, nickel, copper and manganese (Zafar et al., 2005). The metal/metal oxide may be present in various forms, but most studies so far have assumed the use of particles with diameter 100-500 μm. In order to move particles between the two reactors, the particles are fluidised. This method also ensures efficient heat and mass transfer between the gases and the particles. A critical issue is the long-term mechanical and chemical stability of the particles that have to undergo repeated cycles of oxidation and reduction, to minimize the make-up requirement. When a chemical looping cycle is used in a gas turbine cycle, the mechanical strength for crushing and the filtration system is important to avoid damaging carry-over to the turbine.

The temperature in the reactors, according to available information in the literature, may be in the range 800 to 1200°C. NO_x formation at these typical operating temperatures will always be low. The fuel conversion in the reduction reactor may not be complete, but it is likely (Cho et al., 2002) that the concentrations of methane and CO when burning natural gas are very small. In order to avoid deposit of carbon in the reduction reactor, it is necessary to use some steam together with the fuel.

The chemical looping principle may be applied either in a gas turbine cycle with pressurized oxidation and reduction reactors, or in a steam turbine cycle with atmospheric pressure in the reactors. In the case of a gas turbine cycle, the oxidation reactor replaces the combustion chamber of a conventional gas turbine. The exothermic oxidation reaction provides heat for increasing the air temperature entering the downstream expansion turbine. In addition, the reduction reactor exit stream may also be expanded in a turbine together with steam production for power generation. The cooled low pressure CO_2 stream will then be compressed to pipeline pressure. Another option is to

generate steam using heat transfer surfaces in the oxidation reactor. Current Circulating Fluidised Bed combustion technology operating at atmospheric pressure in both the oxidation and reduction stages necessitates the use of a steam turbine cycle for power generation. Using natural gas as fuel in a chemical looping combustion cycle which supplies a gas turbine combined cycle power plant and delivering CO_2 at atmospheric pressure, the potential for natural gas fuel-to-electricity conversion efficiency is estimated to be in the range 45-50% (Brandvoll and Bolland, 2004). Work on chemical looping combustion is currently in the pilot plant and materials research stage.

3.4.7 Status and outlook

Oxy-fuel combustion applied to furnaces, process heaters, boilers and power generation systems is feasible since no technical barriers for its implementation have been identified. Early use of this capture technology is likely to address applications involving indirect heating in power generation and process heating (Section 3.4.2), since these options involve the minimal modification of technologies and infrastructure that have hitherto been already developed for the combustion of hydrocarbon or carbonaceous fuels in air. However, several novel applications proposed for direct heating in steam turbine cycles or gas turbine cycles for power generation (Sections 3.4.3 and 3.4.4) still require the development of new components such as oxy-fuel combustors, higher temperature tolerant components such as CO_2 and H_2O based turbines with blade cooling, CO_2 compressors and high temperature ion transport membranes for oxygen separation. As for Chemical Looping Combustion, it is still at an early stage of development today.

The potential for thermal efficiencies for oxy-fuel cycles with CO_2 capture, assuming the current state of development in power plant technology, is depicted in Figures 3.6 and 3.7. Power generation from pulverised coal fired systems, using supercritical steam conditions presently operate at efficiencies around 45% (LHV), while projections to the 2010-2020 time frame are predicting efficiencies above 50% (IEA, 2004) for plants using ultra-supercritical steam conditions. An increase in efficiency of more than 5% points can therefore be expected for future oxy-fuel capture systems based on coal firing that could potentially match the best efficiencies realisable today for pulverised coal-fired plants without CO_2 capture. Similarly, natural gas fired combined cycles will have efficiencies of 65 % in 2020 (IEA GHG, 2000b and up from current efficiencies between 55 and 58%), which will enable plant efficiencies for natural gas fired oxy-fuel cycles with CO_2 capture above 50%. The energy penalty for producing oxygen is by far the most important cause for reduced efficiency in an oxy-fuel cycle compared to a conventional power plant.

Current technology development envisages very high efficiency separation of NO_x, SO_x, Hg, as part of the CO_2 compression and purification system. Improved separation efficiencies of these contaminants are possible based on further process and heat integration in the power cycle.

Current cryogenic oxygen technology is showing continuing cost reduction based on improved compressor efficiencies, more efficient process equipment and larger scale plants. The new high temperature oxygen membrane could significantly improve power generation efficiency and reduce capital cost.

Future oxy-fuel demonstration plants could be based on retrofits to existing equipment such as process heaters, and boilers, in order to minimize development costs and achieve early market entry. In this respect, power systems of reference for oxy-fuel combustion capture are mainly the steam based pulverised coal and natural gas fired plants that currently represent up to 1468 GWe, or 40% (IEA WEO, 2004) of the existing global infrastructure (see also Section 3.1.2.3). Several demonstration units may be expected within the next few years particularly in Europe, USA, Canada and Australia where active research initiatives are currently underway. As these

developments proceed and the technologies achieve market penetration they may become competitive relative to alternate options based on pre and post-combustion CO_2 capture. A significant incentive to the development of oxy-fuel combustion technology, as well as for pre and post-combustion capture technologies, is the introduction of environmental requirements and/or fiscal incentives to promote CO_2 capture and storage.

3.5 Pre-combustion capture systems

3.5.1 Introduction

A pre-combustion capture process typically comprises a first stage of reaction producing a mixture of hydrogen and carbon monoxide (syngas) from a primary fuel. The two main routes are to add steam (reaction 1), in which case the process is called "steam reforming", or oxygen (reaction 2) to the primary fuel. In the latter case, the process is often called "partial oxidation" when applied to gaseous and liquid fuels and "gasification" when applied to a solid fuel, but the principles are the same.

Steam Reforming

$$C_xH_y + xH_2O \Leftrightarrow xCO + (x+y/2)H_2 \qquad \Delta H +ve \qquad (1)$$

Partial Oxidation

$$C_xH_y + x/2O_2 \Rightarrow xCO + y/2H_2 \qquad \Delta H -ve \qquad (2)$$

This is followed by the "shift" reaction to convert CO to CO_2 by the addition of steam (reaction 3):

Water Gas Shift Reaction

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad \Delta H \text{ -41 kJ/mol} \qquad (3)$$

Finally, the CO_2 is removed from the CO_2/H_2 mixture. The concentration of CO_2 in the input to the CO_2/H_2 separation stage can be in the range 15-60% (dry basis) and the total pressure is typically 2-7 MPa. The separated CO_2 is then available for storage.

It is possible to envisage two applications of pre-combustion capture. The first is in producing a fuel (hydrogen) that is essentially carbon-free. Although the product H_2 does not need to be absolutely pure and may contain low levels of methane, CO or CO_2, the lower the level of carbon-containing compounds, the greater the reduction in CO_2 emissions. The H_2 fuel may also contain inert diluents, such as nitrogen (when air is typically used for partial oxidation), depending on the production process and can be fired in a range of heaters, boilers, gas turbines or fuel cells.

Secondly, pre-combustion capture can be used to reduce the carbon content of fuels, with the excess carbon (usually removed as CO_2) being made available for storage. For example, when using a low H:C ratio fuel such as coal it is possible to gasify the coal and to convert the syngas to liquid Fischer-Tropsch fuels and chemicals which have a higher H:C ratio than coal. In this section, we consider both of these applications.

This section reports on technologies for the production of H_2 with CO_2 capture that already exist and those that are currently emerging. It also describes enabling technologies that need to be developed to enhance the pre-combustion capture systems for power, hydrogen or synfuels and chemicals production or combination of all three.

3.5.2 Existing technologies

3.5.2.1 Steam reforming of gas and light hydrocarbons

Steam reforming is the dominant technology for hydrogen production today and the largest single train plants produce up to 480 t/day of hydrogen. The primary energy source is often natural gas, when the process is referred to as steam methane reforming, or SMR, but can also be other light hydrocarbons, such as naphtha. The process begins with the removal of sulphur compounds from the feed, since these are poisons to the current nickel based catalyst, and then steam is added. The reforming reaction (1), which is endothermic, takes place over a catalyst at high temperature (800-900°C). Heat is supplied to the reactor tubes by burning part of the fuel (secondary fuel). The reformed gas is cooled in a waste heat boiler which generates the steam needed for the reactions and passed into the CO shift system. Shift reactors in one or two stages are used to convert most of the CO in the syngas to CO_2 (Reaction 3, which is exothermic). The conventional two-stage CO conversion reduces the CO concentration in syngas (or in hydrogen) down to 0.2-0.3 %. High temperature shift reactors operating between 400°C and 550°C and using an iron-chromium catalyst leave between 2% and 3% CO in the exit gas (dry basis). Copper based catalyst can be used at temperatures from 180°C to 350°C and leave from 0.2% to 1% CO in the exhaust. Lower CO content favours higher CO_2 recovery. The gas is then cooled and hydrogen is produced by a CO_2/H_2 separation step. Until about 30 years ago, the CO_2 was removed using a chemical (solvent) absorption process such as an amine or hot potassium carbonate and was rejected to atmosphere as a pure stream from the top of the regenerator. There are many of these plants still in use and the CO_2 could be captured readily.

Modern plants, however, use a pressure swing adsorber (PSA), where gases other than H_2 are adsorbed in a set of switching beds containing layers of solid adsorbent such as activated carbon, alumina and zeolites (see the fuller description of PSA in Section 3.5.2.9). The H_2 exiting the PSA (typically ~ 2.2 MPa) can have a purity of up to 99.999%, depending on the market need. The CO_2 is contained in a stream, from the regeneration cycle, which contains some methane and H_2. The stream is used as fuel in the reformer where it is combusted in air and the CO_2 ends up being vented to atmosphere in the reformer flue gas. Hence, to capture CO_2 from modern SMR plants would require one of the post-combustion processes described above in Section 3.3. Alternatively, the PSA system could be designed not only for high recovery of pure H_2 but also to recover pure CO_2 and have a fuel gas as the third product stream.
In a design study for a large modern plant (total capacity 720 tonne/d H_2), the overall efficiency of making 6.0 MPa H_2 from natural gas with CO_2 vented i.e. without CO_2 capture, is estimated to be 76%, LHV basis, with emissions of 9.1 kg CO_2 per kg H_2 (IEA GHG, 1996). The process can be modified (at a cost) to provide a nearly pure CO_2 co-product. One possibility is to remove most of the CO_2 from the shifted, cooled syngas in a "wet" CO_2 removal plant with an appropriate amine solvent. In this case the CO_2-deficient syngas exiting the amine scrubber is passed to a PSA unit from which relatively pure H_2 is recovered, and the PSA purge gases are burned along with additional natural gas to provide the needed reformer heat. The CO_2 is recovered from the amine solvent by heating and pressurized for transport. Taking into account the power to compress the CO_2 (to 11.2 MPa) reduces the efficiency to about 73% and the emission rate to 1.4 kg CO_2 per kg H_2, while the CO_2 removal rate is 8.0 kg CO_2 per kg H_2.

3.5.2.2 Partial oxidation of gas and light hydrocarbons

In the partial oxidation (POX) process (reaction 2), a fuel reacts with pure oxygen at high pressure. The process is exothermic and occurs at high temperatures (typically 1250-1400°C). All the heat required for the syngas reaction is supplied by the partial combustion of the fuel and no external

heat is required. As with SMR, the syngas will be cooled, shifted and the CO_2 removed from the mixture. The comments made on the separation of CO_2 from SMR syngas above apply equally to the POX process. POX is a technology in common use today, the efficiency is lower than SMR, but the range of fuels that can be processed is much wider.

For large-scale hydrogen production, the oxygen is supplied from a cryogenic air separation unit (ASU). The high investment and energy consumption of the ASU is compensated by the higher efficiency and lower cost of the gasification process and the absence of N_2 (from the air) in the syngas, which reduces the separation costs considerably. However for pre-combustion de-carbonisation applications, in which the hydrogen would be used as fuel in a gas turbine, it will be necessary to dilute the H_2 with either N_2 or steam to reduce flame temperature in the gas turbine combustor and to limit NO_x emission levels. In this case the most efficient system will use air as the oxidant and produce a H_2/N_2 fuel mixture (Hufton et al. 2005)

3.5.2.3 Auto-thermal reforming of gas and light hydrocarbons

The autothermal reforming (ATR) process can be considered as a combination of the two processes described above. The heat required in the SMR reactor is generated by the partial oxidation reaction (2) using air or oxygen, but because steam is supplied to the reactor as well as excess natural gas, the endothermic reforming reaction (1) occurs, in a catalytic section of the reactor downstream of the POX burner. The addition of steam enables a high conversion of fuel to hydrogen at a lower temperature. Operating temperatures of the autothermal process are typically 950-1050°C, although this depends on the design of the process. An advantage of the process, compared to SMR, is the lower investment cost for the reactor and the absence of any emissions of CO_2 since all heat release is internal, although this is largely offset by investment and operating cost for the oxygen plant. The range of fuels that can be processed is similar to the SMR process, but the feed gas must be sulphur free. CO_2 capture is accomplished as described above for the steam methane reforming.

3.5.2.4 Gas Heated Reformer

Each of the three syngas generation technologies, SMR, ATR and POX produce high temperature gas which must be cooled, producing in each case a steam flow in excess of that required by the reforming and shift reactions. It is possible to reduce this excess production by, for example, using preheated air and a pre-reformer in an SMR plant. Another technique is to use the hot syngas, leaving the primary reactor, as the shell-side heating fluid in a tubular steam/hydrocarbon reforming reactor which can operate in series, or in parallel, with the primary reactor (Abbott et al., 2002). The addition of a secondary gas heated reformer will increase the hydrogen production by up to 33%, and eliminate the excess steam production. The overall efficiency is improved and specific capital cost is reduced typically by 15%. Again, CO_2 capture is accomplished as described previously for steam methane reforming.

3.5.2.5 Gasification of coal, petroleum residues, or biomass

Gasification (see Figure 3.14) is a chemical process aimed at making high-value products (chemicals, electricity, clean synthetic fuels) out of low-value solid feedstocks e.g., coal, oil refining residues, or biomass. Gasification is basically partial oxidation (reaction 2), although steam is also supplied to the reactor in most processes. Fixed bed, fluidized bed or entrained flow gasifiers can be used. These can have very different characteristics with respect to oxidant (air or O_2), operating temperature (up to 1350^{o}C), operating pressure (0.1 to 7 MPa), feed system (dry or water slurry), syngas cooling method (water quench or via radiative and convective heat exchangers) and gas cleanup system deployed. These alternative design options determine the fraction of feedstock converted to syngas, syngas composition, and cost. Because economics depend strongly on scale,

gasification is generally considered suitable only for large plants. The gasifier output contains CO, H_2, CO_2, H_2O, and impurities (e.g., N_2, COS, H_2S, HCN, NH_3, volatile trace minerals and Hg) that must be managed appropriately.

Figure 3.14. Simplified schematic of a gasification process showing options with CO_2 capture and electricity, hydrogen or chemical production.

A world-wide survey of commercial gasification projects identified 128 operating gasification plants with 366 gasifiers producing 42,700 MW_t of syngas (NETL-DOE, 2002 and Simbeck, 2001a). There are also about 24,500 MW_t of syngas for projects under development or construction, with 4,000 - 5,000 MW_t of syngas added annually. The feedstocks are mainly higher rank coals and oil residues. Most commercial gasification growth for the last 20 years has involved entrained-flow gasifiers, for which there are three competing systems on the market. Recent commercial gasification development has been mainly with industrial ammonia production, industrial polygeneration (in which clean syngas is used to make electricity and steam along with premium syngas chemicals), and integrated gasification combined cycle (IGCC) power plants. Commercial experience with biomass gasification and fluidised bed gasification has been limited

CO_2 capture technology is well established for gasification systems that make chemicals and synthetic fuels (NETL-DOE, 2002). Gasification-based NH_3 plants (many in China) include making pure H_2 and CO_2 separation at rates up to 3500 tonnes/day CO_2 per plant. South African plants making Fischer-Tropsch fuels and chemicals and a North Dakota plant making synthetic natural gas (SNG) from coal also produce large streams of nearly pure CO_2. Figure 3.15 shows a picture of the North Dakota gasification plant in which 3.3 million tonnes/y CO_2 is captured using a refrigerated methanol based, physical solvent scrubbing process (Rectisol process, see Section 3.5.2.11 and Table 3.2). Most of this captured CO_2 is vented and about 1.5 million tonnes/y of this stream is currently pipelined to the Weyburn, Canada enhanced oil recovery and CO_2 storage project (see Chapter 5).

Table 3.2. Common solvents used for the removal of CO_2 from shifted syngas in pre-combustion capture processes.

Figure 3.15. North Dakota coal gasification plant with 3.3 million tonnes/y of CO_2 capture using a cold methanol, physical solvent process (cluster of 4 tall columns in the middle of the picture represent the H_2S and CO_2 capture processes; part of the captured stream is used for EOR with CO_2 storage in Weyburn, Saskatchewan, Canada).

When CO_2 capture is an objective, O_2-blown and high-pressure systems are preferred because of the higher CO_2 partial pressures. De-carbonization via gasification entails lower energy penalties for CO_2 capture than does post-combustion capture when considering only the separation stage, because the CO_2 can be recovered at partial pressures up to 3 orders of magnitude higher. This greatly reduces CO_2 absorber size, solvent circulation rates and CO_2 stripping energy requirements. However, additional energy penalties are incurred in shifting the CO in the syngas to CO_2 and in other parts of the system (see examples for IGCC plant with CO_2 capture in Figures 3.6 and 3.7). Recent analyses for bituminous coals (see, for example, IEA GHG, 2003) suggest using simple high-pressure entrained-flow gasifiers with water slurry feed and direct water quench followed by "sour" (sulphur-tolerant) shift reactors, and finally co-removal of CO_2 and H_2S by physical absorption. With sour shifting, hot raw syngas leaving the gasifier requires only one cooling cycle and less processing. Oxygen requirements increase for slurry fed gasifiers and conversion efficiencies decline with higher cycle efficiency losses with quench cooling. Similar trends are also

noted with a shift from bituminous to lower rank sub-bituminous coal and lignite (Breton and Amick, 2002). Some analyses (e.g., Stobbs, 2005) suggest that the advantages of pre-combustion over post-combustion de-carbonization may be small or disappear for such coals converted with entrained-flow gasifiers. High-pressure, fluidised-bed gasifiers may be better suited for use with low-rank coals, biomass, and various carbonaceous wastes. Although there are examples of successful demonstration of such gasifiers (e.g., the high temperature Winkler, Renzenbrink et al., 1998), there has been little commercial-scale operating experience.

The H_2S in syngas must be removed to levels of tens of ppmv for IGCC plants for compliance with SO_2 emissions regulations and to levels much less than 1 ppmv for plants that make chemicals or synthetic fuels, so as to protect synthesis catalysts. If the CO_2 must be provided for storage in relatively pure form, the common practice would be to recover first H_2S (which is absorbed more readily than CO_2) from syngas (along with a small amount of CO_2) in one recovery unit, followed by reduction of H_2S to elemental sulphur in a Claus plant and tail gas cleanup, and subsequent recovery of most of the remaining CO_2 in a separate downstream unit. An alternative option is to recover sulphur in the form of sulphuric acid (McDaniel and Hormick, 2002). If H_2S/CO_2 co-storage is allowed, however, it would often be desirable to recover H_2S and CO_2 in the same physical absorption unit, which would lead to moderate system cost savings (IEA GHG, 2003; Larson and Ren, 2003; Kreutz et al., 2005) especially in light of the typically poor prospects for selling byproduct sulphur or sulphuric acid. Although co-storage of H_2S and CO_2 is routinely pursued in Western Canada as an acid gas management strategy for sour natural gas projects (Bachu and Gunter, 2005), it is not yet clear that co-storage would be routinely viable at large scales—a typical gasification based energy project would involve an annual CO_2 storage rate of 1-4 million tonnes per year, whereas the total CO_2 storage rate for all 48 Canadian projects is presently only 0.48 million tonnes/y (Bachu and Gunter, 2005).

3.5.2.6 Integrated gasification combined cycle (IGCC) for power generation

In a coal IGCC, syngas exiting the gasifier is cleaned of particles, H_2S, and other contaminants and then burned to make electricity via a gas turbine/steam turbine combined cycle. The syngas is generated and converted to electricity at the same site, both to avoid the high cost of pipeline transport of syngas (with a heating value only ~1/3 of that for natural gas) and to exploit cost-effectively opportunities for making extra power in the combined cycle's steam turbine using steam from syngas cooling. The main drivers for IGCC development were originally the prospects of exploiting continuing advances in gas turbine technology, the ease of realizing low levels of air-pollutant emissions when contaminants are removed from syngas, and greatly reduced process stream volumes compared to flue gas streams from combustion which are at low pressure and diluted with nitrogen from air.

Since the technology was initially demonstrated in the 1980s, about 4 GW_e of IGCC power plants has been built. Most of this capacity is fueled with oil or petcoke; less than 1 GWe of the total is designed for coal (IEA CCC, 2005) and with 3 out of 4 plants currently operating on coal and/or petcoke. This experience has demonstrated IGCC load-following capability, although the technology will probably be used mainly in base load applications. All coal-based IGCC projects have been subsidised, whereas only the Italian oil-based IGCC projects have been subsidised. Other polygeneration projects in Canada, the Netherlands, and the United States, as well as an oil-based IGCC in Japan, have not been subsidized (Simbeck, 2001a).

IGCC has not yet been deployed more widely because of strong competition from the natural gas combined cycle (NGCC) wherever natural gas is readily available at low prices, because coal-based IGCC plants are not less costly than pulverised coal fired steam-electric plants, and because of

availability (reliability) concerns. IGCC availability has improved in recent years in commercial-scale demonstration units (Wabash River Energy, 2000; McDaniel and Hornick, 2002). Also, availability has been better for industrial polygeneration and IGCC projects at oil refineries and chemical plants where personnel are experienced with the chemical processes involved. The recent rise in natural gas prices in the USA has also increased interest in IGCC.

Because of the advantages for gasification of CO_2 capture at high partial pressures discussed above, IGCC may be attractive for coal power plants in a carbon-constrained world (Karg, 2004). CO_2 capture for pre-combustion systems is commercially ready, however, no IGCC plant incorporating CO_2 capture has yet been built. With current technology, average estimates of the energy penalties and the impact of increased fuel use for CO_2 removal are compared with other capture systems in Figures 3.6 and 3.7 and show the prospective potential of IGCC options. The data in Figures 3.6 and 3.7 also show that some IGCC options may be different from others (i.e. slurry fed and quench cooled versus dry feed and syngas cooling) and their relative merits in terms of the capital cost of plant and the delivered cost of power are discussed in Section 3.7.

3.5.2.7 Hydrogen from coal with CO_2 capture

Relative to intensively studied coal IGCC technology with CO_2 capture, there are few studies in the public domain on making H_2 from coal via gasification with CO_2 capture (NRC, 2004; Parsons 2002a, b; Gray and Tomlinson 2003; NRC 2004; Chiesa et al., 2005; Kreutz et al., 2005), even though this H_2 technology is well established commercially, as noted above. With commercial technology, H_2 with CO_2 capture can be produced via coal gasification in a system similar to a coal IGCC plant with CO_2 capture. In line with the design recommendations for coal IGCC plants described above (IEA GHG, 2003), what follows is the description from a design study of a coal H_2 system that produces, using best available technology, 1070 MW_t of H_2 from high-sulphur (3.4%) bituminous coal (Chiesa et al., 2005; Kreutz et al., 2005). In the base case design, syngas is produced in an entrained flow quench gasifier operated at 7 MPa. The syngas is cooled, cleaned of particulate matter, and shifted (to primarily H_2 and CO_2) in sour water gas shift reactors. After further cooling, H_2S is removed from the syngas using a physical solvent (Selexol). CO_2 is then removed from the syngas, again using Selexol. After being stripped from the solvents, the H_2S is converted to elemental S in a Claus unit and a plant provides tail gas cleanup to remove residual sulphur emissions; and the CO_2 is either vented or dried and compressed to 150 atm for pipeline transport and underground storage. High purity H_2 is extracted at 6 MPa from the H_2-rich syngas via a pressure swing adsorption (PSA) unit. The PSA purge gas is compressed and burned in a conventional gas turbine combined cycle, generating 78 MW_e and 39 MW_e of electricity in excess of onsite electricity needs in the without and with CO_2 capture cases, respectively. For this base case analysis, the effective efficiency of H_2 manufacture was estimated to be 64% with CO_2 vented and 61% with CO_2 captured, while the corresponding emission rates are 16.9 kg CO_2 and 1.4 kg CO_2 per kg H_2, respectively. For the capture case, the CO_2 removal rate was 14.8 kg CO_2 per kg H_2. Various alternative system configurations were explored. It was found that there are no thermodynamic or cost advantages from increasing the electricity/H_2 output ratio, so this ratio would tend to be determined by relative market demands for electricity and H_2. One potentially significant option for reducing the cost of H_2 with CO_2 capture to about the same level as with CO_2 vented involves H_2S/CO_2 co-capture in a single Selexol unit, as discussed above.

3.5.2.8 Carbon-based fluid fuels and multi-products

As discussed in Chapter 2, clean synthetic high H/C ratio fuels can be made from syngas via gasification of coal or other low H/C ratio feedstocks. Potential products include synthetic natural gas, Fischer-Tropsch diesel/gasoline, dimethyl ether, methanol, and gasoline from methanol via the

Mobil process. A by product is typically a stream of relatively pure CO_2 that can be captured and stored.

Coal derived Fischer-Tropsch synfuels and chemicals have been produced at commercial scale in South Africa; coal methanol is produced in China and at one US plant; and coal SNG is produced at a North Dakota (US) plant (NETL-DOE, 2002). Since 2000, 1.5 million t/y of CO_2 from the North Dakota synthetic natural gas plant (see Figure 3.15) have been transported by pipeline, 300 km to the Weyburn oil field in Saskatchewan, Canada for enhanced oil recovery with CO_2 storage.

Synfuel manufacture involves O_2–blown gasification to make syngas, gas cooling, gas cleanup, water gas shift , and acid gas (H_2S/CO_2) removal. Subsequently cleaned syngas is converted catalytically to fuel in a synthesis reactor, and unconverted syngas is separated from the liquid fuel product. At this point either most unconverted gas is recycled to the synthesis reactor to generate additional liquid fuel and the remaining unconverted gas is used to make electricity for onsite needs, or syngas is passed only once through the synthesis reactor, and all unconverted syngas is used for other purposes, e.g., to make electricity for sale to the electric grid as well as for onsite use. The latter *once through* (OT) option is often more competitive as a technology option (Williams, 2000; Gray and Tomlinson, 2001; Larson and Ren, 2003; Celik et al., 2005).

New slurry-phase synthesis reactors make the once through configuration especially attractive for CO-rich (e.g., coal-derived) syngas by making possible high once through conversion. For once through systems, a water gas shift reactor is often placed upstream of the synthesis reactor to generate the H_2/CO ratio that maximizes synfuel conversion in the synthesis reactor. It is desirable to remove most CO_2 from shifted syngas to maximize synthetic fuel conversion. Also, because synthesis catalysts are extremely sensitive to H_2S and various trace contaminants, these must be removed to very low levels ahead of the synthesis reactor. Most trace metals can be removed at low cost using an activated carbon filter. CO_2 removal from syngas upstream of the synthesis reactor is a low-cost partial de-carbonization option, especially when H_2S and CO_2 are co-captured and co-stored as an acid gas management strategy (Larson and Ren, 2003). Further de-carbonization can be realized in OT systems, at higher incremental cost, by adding additional shift reactors downstream of the synthesis reactor, recovering the CO_2, and using the CO_2-depleted, H_2-rich syngas to make electricity or some mix of electricity plus H_2 in a "polygeneration" configuration (see Figure 3.16). The relative amounts of H_2 and electricity produced would depend mainly on relative demands, as there do not seem to be thermodynamic or cost advantages for particular H_2/electricity production ratios (Chiesa et al., 2005; Kreutz et al., 2005). When syngas is de-carbonized both upstream and downstream of the synthesis reactor (see Figure 3.16) it is feasible to capture and store as CO_2 up to 90% of the carbon in the original feedstock except that contained in the synthetic fuel produced.

Figure 3.16. Making liquid fuel, electricity, and hydrogen from coal via gasification, with CO_2 capture and storage.

An example of such a system (Celik et al., 2005) is one making from coal, 600 MW of dimethyl ether (containing 27% of coal input energy and 20% of coal input carbon) plus 365 MW of electricity (no H_2). For this system the CO_2 storage rate (equivalent to 74% of C in coal) is 3.8 million tonnes/y (39% from upstream of the synthesis reactor). For this system the estimated fuel cycle-wide GHG emissions for dimethyl ether are 0.9 times those for crude oil-derived diesel and those for electricity are 0.09 times those for a 43% efficient coal fired power plant with CO_2 vented.

3.5.2.9 Pressure Swing Adsorption

Pressure Swing Adsorption (PSA) is the system of choice for the purification of syngas, where high purity H_2 is required. However, it does not selectively separate CO_2 from the other waste gases and so for an SMR application the CO_2 concentration in the waste gas would be 40-50% and require further upgrading to produce pure CO_2 for storage. Simultaneous H_2 and CO_2 separation is possible by using an additional PSA section to remove the CO_2 prior to the H_2 separation step, such as the Air Products Gemini Process (Sircar, 1979).

The PSA process is built around adsorptive separations of cyclic character. The cycles consist of two basic steps: adsorption, in which the more adsorbable species are selectively removed from the feed gas and regeneration (desorption), when these species are removed from the adsorbent so that it can be ready for the next cycle. It is possible to obtain useful products during both adsorption and regeneration. The principal characteristic of PSA processes is the use of a decrease in pressure and/or the purge by a less adsorbable gas to clean the adsorbent bed. Apart from adsorption and regeneration, a single commercial PSA cycle consists of a number of additional steps, including co- and counter current pressurization, pressure equalization and co- and counter current depressurization. A detailed description of the PSA technique, along with its practical applications can be found elsewhere (Ruthven et al., 1994).

3.5.2.10 Chemical Solvent Processes

Chemical solvents are used to remove CO_2 from syngas at partial pressures below about 1.5 MPa (Astarita, 1983) and are similar to those used in post combustion capture (see Section 3.3.2.1). The solvent removes CO_2 from the shifted syngas, by means of a chemical reaction, which can be reversed by pressure reduction and heating. The tertiary amine methyldiethanolamine (MDEA, see Table 3.2) is widely used in modern industrial processes, due to the high CO_2 loading possible and the low regenerator heating load, relative to other solvents. Hot potassium carbonate (the most common commercial version of which is known as Benfield) was used for CO_2 removal in most hydrogen plants until about 15 years ago.

3.5.2.11 Physical Solvent Processes

Physical solvent (or absorption) processes are mostly applicable to gas streams which have a high CO_2 partial pressure and/or a high total pressure. They are often used to remove the CO_2 from the mixed stream of CO_2 and H_2 that comes from the shift reaction in pre-combustion CO_2 capture processes such as product from partial oxidation of coal and heavy hydrocarbons.

The leading physical solvent processes are shown in Table 3.2. The regeneration of solvent is carried out by release of pressure at which CO_2 evolves from the solvent, in one or more stages. If a deeper regeneration is required the solvent would be stripped by heating. The process has low energy consumption, as only the energy for pressurising the solvent (liquid pumping) is required.

The use of high sulphur fossil fuels in a pre-combustion capture process results in syngas with H_2S. These acid gas components must both be removed. If transport and storage of mixed CO_2 and H_2S is possible then both components can be removed together. Sulfinol was developed to achieve significantly higher solubilities of acidic components compared to amine solvents, without added problems of excessive corrosion, foaming, or solution degradation. It consists of a mixture of sulfolane (tetrahydrothiophene 1,1-dioxide), an alkanolamine and water in various proportions depending on the duty. If pure CO_2 is required, then a selective process is required using physical solvents - often Rectisol or Selexol. The H_2S must be separated at sufficiently high concentration (generally >50%) to be treated in a sulphur recovery plant.

3.5.2.12 Effect on other pollutants

Pre-combustion capture includes reforming, partial oxidation or gasification. In order to maintain the operability of the catalyst of reformers, sulphur (H_2S) has to be removed prior to reforming. In gasification, sulphur can be captured from the syngas, and in the case when liquid or solid fuels are gasified, particulates, NH_3, COS and HCN are also present in the system that need to be removed. In general, all of these pollutants can be removed from a high-pressure fuel gas prior to combustion, where combustion products are diluted with nitrogen and excess oxygen. In the combustion of hydrogen or a hydrogen-containing fuel gas, NO_x may be formed. Depending upon combustion technology and hydrogen fraction, the rate at which NO_x is formed may vary. If the volumetric fraction of hydrogen is below approximately 50-60%, NO_x formation is at the same level as for natural gas dry low-NO_x systems (Todd, 2001).

In general, with the exception of H_2S that could be co-removed with CO_2, other pollutants identified above are separated in additional pre-treatment operations, particularly in systems that gasify liquid or solid fuels. High temperature pre-treatment operations for these multi-pollutants that avoid cooling of the syngas have the advantage of improving the cycle efficiency of the overall gasification process, but these separation processes are currently not commercially demonstrated. Although it is not yet regulated as a "criteria pollutant", mercury (Hg), is currently the focus of considerable concern as a pollutant from coal power systems. For gasification systems Hg can be recovered from syngas at ambient temperatures at very low cost compared to Hg recovery from flue gases (Klett and Rutkowski, 2001).

3.5.3 Emerging technologies

Emerging options in both natural gas reforming and coal gasification incorporate novel combined reaction/separation systems such as sorption enhanced reforming and sorption enhanced water gas shift, membrane reforming and membrane water gas shift. Finally there is a range of technologies that make use of the carbonation of CaO for CO_2 capture.

3.5.3.1 Sorption Enhanced Reaction

A concept called Sorption Enhanced Reaction (SER) uses a packed bed containing a mixture of a catalyst and a selective adsorbent to remove CO_2 from a high temperature reaction zone, thus driving the reaction to completion. (Hufton et al., 1999). The adsorbent is periodically regenerated by using a pressure swing, or temperature swing adsorption system with steam regeneration. (Hufton et al., 2005)

High temperature CO_2 adsorbents such as hydrotalcites (Hufton et al., 1999) or lithium silicate (Nakagawa, 1998) can be mixed with a catalyst to promote either the steam methane reforming reaction (Reaction 1) or water gas shift reaction (Reaction 3) producing pure hydrogen and pure CO_2 in a single process unit. The continuous removal of the CO_2 from the reaction products by adsorption shifts each reaction towards completion.

The SER can be used to produce hydrogen at 400 C to 600 C to fuel a gas turbine combined cycle power generation system. A design study based on a General Electric 9FA gas turbine with hot hydrogen, produced from an air blown ATR with a sorption enhanced water gas shift reactor, gave a theoretical net efficiency of 48.3% with 90% CO_2 capture at 99% purity and 150 bar pressure (Hufton et al., 2005). The process is currently at the pilot plant stage.

3.5.3.2 Membrane reactors for hydrogen production with CO_2 capture

Inorganic membranes with operation temperatures up to 1000°C offer the possibility of combining reaction and separation of the hydrogen in a single stage at high temperature and pressure to overcome the equilibrium limitations experienced in conventional reactor configurations for the production of hydrogen. The combination of separation and reaction in membrane steam reforming and/or membrane water gas shift offers higher conversion of the reforming and/or shift reactions due to the removal of hydrogen from these equilibrium reactions as shown in Reactions (1) and (3) respectively. The reforming reaction is endothermic and can, with this technique, be forced to completion at lower temperature than normal (typically 500 to 600°C). The shift reaction being exothermic can be forced to completion at higher temperature (500 to 600°C).

Another reason to incorporate H_2 separation membranes in the hydrogen production system, is that CO_2 is also produced without the need for additional separation equipment. Membrane reactors allow one-step reforming, or a single intermediate water gas shift reaction, with hydrogen separation (the permeate) leaving behind a retentate gas which is predominantly CO_2 and a small amount of non-recovered hydrogen and steam. This CO_2 remains at the relatively high pressure of the reacting system (see figure 3.17). Condensation of the steam leaves a concentrated CO_2 stream at high pressure, reducing the compression energy for transport and storage. Membrane reforming will benefit from high pressure operation due to the increased H_2 partial pressure differential across the membrane which is the driving force for hydrogen permeation. Therefore membrane reactors are also seen as a good option for pre-combustion de-carbonisation where a low-pressure hydrogen stream for fuel gas and a high pressure CO_2 rich stream for transport and storage are required. The use of the membrane reformer reactor in a gas turbine combined cycle means that the hydrogen needs to be produced at such pressure that the significant power consumption for the hydrogen compression is avoided. This could be done by increasing the operating pressure of the membrane reactor or by using a sweep gas, for instance steam, at the permeate side of the membrane (Jordal et al., 2003).

Figure 3.17. Operating principle of a membrane reactor.

For these membrane reactor concepts, a hydrogen selective membrane capable of operating in a high-temperature, high-pressure environment is needed. In the literature a number of membrane types have been reported that have these capabilities and these are listed in Table 3.3. Micro-porous inorganic membranes based upon surface diffusion separation exhibit rather low separation factors (e.g., H_2/CO_2 separation factor of 15). However, the separation ability of the current commercially available gamma-alumina and silica micro porous membranes (which have better separation factors, up to 40) depends upon the stability of the membrane pore size, which is adversely affected by the presence of steam in the feed streams. The dense ceramic membranes based on inorganic perovskite oxides (also called proton conducting) need high temperatures, higher than 800°C, to achieve practical hydrogen flux rates. Palladium-based dense membranes are also known for their high hydrogen selectivity and permeability over other gases in the temperature range 300 and 600°C that is appropriate for these two reactions. Palladium alloy tubes have been available for several decades, but for CCS applications they are too expensive due to the membrane thickness needed for structural stability and consequently low hydrogen flux rates. In order to be suitable for the target application, a hydrogen separation membrane must have adequate selectivity and flux rate and must be stable in the reducing coal gas or fuel reforming environment containing steam and hydrogen sulphide.

Table 3.3. Membrane materials, operating conditions and characteristics for H_2 separation.

A number of membrane reactor developments have been reported for hydrogen production with CO_2 capture. Several groups have evaluated methane steam reforming membrane reactors based on palladium alloy membranes (Middleton 2002, Damle 2001). These evaluations showed that membrane reactors could achieve 90% CO_2 recovery and that at this moment the projected cost is nearly identical to that for a conventional system. However, a reduction of cost can be achieved either by reduction in material cost of the membrane or by increase of the permeability. Similar evaluations of membrane reactors for the shift conversion and separation of CO_2 from syngas produced from heavy feeds by gasification have been reported (Bracht 1997, Middleton 2002 and Lowe 2003). For these gasifier systems the membrane reactors could reduce the costs for capturing CO_2 and the cost reduction would be more significant if they could be made sulphur tolerant.

3.5.3.3 Micro Channel Reformer

Micro reactor technology can be used to produce a SMR, or low temperature air-based POX system using a multi-channel plate-fin heat exchanger, fabricated in stainless steel or high nickel alloy by vacuum brazing or diffusion bonding.

A SMR reactor consists of alternate passages having fins, which are coated with catalyst or porous catalyst insets. Heat is produced by catalytic combustion of fuel gas premixed with air and transferred by conduction to the adjacent passage fed with the steam/hydrocarbon mixture, where the reforming reaction takes place (Babovic et al., 2001). Very compact high efficiency systems can be produced. Although these units are being currently developed by a number of groups for small scale H_2 production for fuel cell applications, they also show promise in larger H_2 plants.

3.5.3.4 Conversion to hydrogen and carbon

Thermal cracking or pyrolysis of methane is the reaction where methane reacts to carbon and hydrogen through:

Methane pyrolysis:

$$CH_4 \rightarrow C + 2\,H_2 \quad (4)$$

The main advantage of the process is that it can potentially yield a clean gas (free of carbon oxides) that could be used directly for power production, but a disadvantage is that the chemical energy from the oxidation of carbon to CO_2 is not released. The cracking reaction is endothermic and so heat has to be supplied to the reaction. If the natural gas is converted fully, the theoretical yield of hydrogen corresponds to 60% of the heating value of the natural gas. The amount of carbon, which can be obtained, corresponds to 49% of the heating value, with the extra 9% of the energy in this calculation being provided as endothermic heat shown by reaction 4 above. Therefore full conversion can be achieved only if heat is supplied from an external source. If full conversion of methane is not achieved, the remaining methane will be combusted to produce heat. There are many different methods under development for reactors based on this principle, including thermal catalytic, thermal non-catalytic and plasma cracking.

In the plasma cracking process natural gas or other hydrocarbons are supplied to a plasma reactor where the hydrocarbons are cracked under pyrolysis conditions (i.e. in absence of oxides, e.g. steam, which can supply oxygen to form CO or CO_2). The plasma arc, for which electricity is used, supplies the heat for the cracking reaction. Advantages of the process are its flexibility with respect to the fuel and the high quality carbon black which can be produced. Two small-scale plasma cracking processes for hydrogen/syngas production have been in development. The Glid Arc process is developed by the Canadian Synergy Technologies Corporation. The second process is the Kvaerner CB&H process. Kvaerner has reported results for a pilot plant producing 1000 Nm^3

hydrogen per hour and 270 kg or 500 kg carbon black using natural gas and aromatic oil respectively (IEA GHG, 2001).

3.5.3.5 *Calcium Oxide based technologies*

There is a range of pre-combustion systems that make use of the carbonation reaction of CaO at high pressures and temperatures, to integrate further the gasification of the fuel (if solid), the shift reaction, and in-situ CO_2 removal with CaO. The overall reaction aimed in the system is:

Carbonation of Calcium Oxide:

$$CaO + C + 2\,H_2O \leftrightarrow CaCO_3 + 2H_2 \quad (5)$$

The regeneration of the sorbent produces pure CO_2 when carried out in a separate reactor by calcining $CaCO_3$. A range of systems can be developed under this general reaction scheme depending on the technology adopted for gasification, carbonation-calcination, hydrogen utilisation route, and storage option for CO_2. The first of these concepts was proposed at the Los Alamos National Laboratory (USA) and is currently under development as the Zero Emission Coal Alliance (ZECA) process. The full system includes (Lackner et al., 2001) a hydro-gasification reactor, solid oxide fuel cell and a technology for mineral carbonation. However, the fuel cell will require more development and mineral carbonation is only at the laboratory investigation stage (see Section 7.2 for a discussion of mineral carbonation).

The HyPrRing process (Lin et al., 2002) is being developed by the Center for Coal Utilization of Japan. It integrates gasification, reforming and in situ CO_2 capture in a single reactor at pressures above 12 MPa and temperature above 650ºC. Projects in Norway using natural gas and in Germany using brown coal (Bandi et al., 2002) are also underway developing pre-combustion systems using capture of CO_2 with CaO. Finally, General Electric (Rizeq, 2002) is developing an innovative system involving the capture of CO_2 in the gasification reactor by a high temperature sorbent and with calcination in a separate reactor by burning part of the fuel with an oxygen carrier.

All these systems are at an early stage of development. Detailed process simulations show that the efficiencies are potentially high because most of the energy employed for sorbent regeneration is effectively transferred to the H_2 generated in reaction (5). The systems are aimed at very large scale generation of electricity and/or H_2 and cement production (from the deactivated sorbent, CaO). However, many uncertainties remain on the performance of the individual units and their practical integration. The main challenge may be the regeneration of the sorbent at very high temperatures ($>900^0$ C), to produce a pure stream of CO_2. Another is the operating conditions to achieve sufficient conversion towards hydrogen, without the use of a catalyst for the shift reaction.

3.5.4 Enabling technologies

The performance and cost of a pre-combustion capture system is linked to the availability of the enabling technologies that complete the system. In this section we consider the availability of industrial systems, to produce heat from the de-carbonised fuel and gas turbines and fuel cells to produce power.

3.5.4.1 Use of decarbonised fuel in industrial systems

The use of hydrogen as a fuel for conventional fired heaters and boilers is considered to be proven and indeed it is practised at certain industrial sites. There is a very large stock of capital equipment of this type and so the use of hydrogen as a fuel might be considered a valuable technology option

in a carbon-constrained world. A study (IEA GHG, 2000c) has looked at the cost of converting an existing refinery to use hydrogen fuel.

3.5.4.2 Use of decarbonised fuel in gas turbine systems

There is extensive commercial experience with hydrogen rich fuel gas firing in gas turbines. For example, General Electric reports over 450,000 hours of operating experience with high hydrogen (52-95% by volume) content fuel gas in gas turbines (Shilling 2003). Unfortunately, most of that experience is for "refinery gas" where methane is the other main component of the fuel gas and is utilized in older lower firing temperature gas turbines, not the state-of-the-art over 1,300°C gas turbines normally considered for large de-carbonization power plants.

Norsk Hydro and General Electric collaborated to perform full-scale combustion system testing for modern gas turbines firing hydrogen rich gas with combustion exit temperatures of above 1,400°C (Todd 2001). The results showed good combustion conditions with low NO_x emission and acceptable hot metal temperatures for mixtures with 54-77% by volume hydrogen with most of the additional gas being nitrogen. Dilution of the hydrogen with nitrogen or steam reduces the NO_x emission.

For pre-combustion capture of CO_2 from natural gas, air-blown gasification or autothermal reforming is usually preferred (IEA GHG, 2000b and Wilkinson, 2002). Nitrogen dilution of the hydrogen required for firing in modern gas turbines comes from the gasification air. High-pressure air is usually extracted from the gas turbine to feed the air-blown gasifier, or autothermal reformer to reduce costs and avoid a separate air compressor. The balance between the amount of air withdrawn from the gas turbine and the amount provided from a separate air compressor is determined by the particular characteristics of the gas turbine used. Some gas turbines can accept a higher ratio of expander to compressor flow, allowing greater volumes of dilution gas or smaller air side draw flow and giving higher power output.

For pre-combustion capture of CO_2 from coal, oxygen-blown gasification is usually preferred (IEA GHG, 2003). Nitrogen dilution of the hydrogen required for firing in modern gas turbines comes from the cryogenic air separation unit (used to make the oxygen; see Section 3.4.5.1). The nitrogen is added to the hydrogen after the gasification, CO shifting and CO_2 capture to reduce the equipment sizes and cost. High-pressure air is usually extracted from the gas turbine to supply a higher than normal pressure cryogenic air separation unit to reduce costs plus air, oxygen and nitrogen compression power. An alternative IGCC scheme that incorporates newly emerging ion transport membranes for oxygen production is also described below in Section 3.5.4.3.

3.5.4.3 Syngas production using oxygen membranes

Oxygen required for a coal-fired integrated gasification combined cycle (IGCC) process (section 3.5.2.6) can be generated in an oxygen transport membrane system by using a heated, high pressure air stream produced by heating the discharge air from the compressor section of a gas turbine (Allam et al., 2002), typically at 1.6 MPa or 420°C, to the precise inlet temperature of the oxygen transport membrane module which is above 700°C. The oxygen, which permeates to the low pressure side passes through a heat recovery section and is compressed to the final pressure of use. The O_2 depleted air leaving the oxygen transport membrane module then enters the gas turbine combustor where it is used to burn fuel before entering the gas turbine expander at the required temperature. Note that due to the necessity to have excess air in a gas turbine to limit turbine inlet temperature, removing one mole of oxygen can be compensated by injection of the equivalent thermal capacity of steam to maintain gas turbine power output. Studies have been carried out (Armstrong et.al., 2002) to compare oxygen transport membrane and cryogenic oxygen production

in an IGCC power plant using coal as fuel The oxygen plant projected cost was reduced by 35% and the power consumption by 37%. A LHV efficiency of 41.8% without CO_2 capture and compression is reported for this cycle compared to 40.9% when a conventional cryogenic oxygen plant is used.

For auto thermal reforming or the partial oxidation of natural gas, if the permeate side of the oxygen transport membrane is exposed to a natural gas plus water vapour stream in the presence of a reforming catalyst, the oxygen will react as it leaves the membrane in an exothermic reaction (Dyer et al., 2001, Carolan et al., 2001), which will provide heat for the endothermic steam/natural gas reforming reaction. The oxygen partial pressure at these highly reducing high temperature conditions is extremely low allowing heated air at close to atmospheric pressure to be used on the feed side of the membrane, while producing a H_2 + CO mixture at high pressure from the permeate side. This system can be used to produce H_2 following CO shift reaction and CO_2 removal.

3.5.4.4 Chemical looping gasification/reforming

The chemical looping concept described in 3.4.6 is being considered for reforming of a fuel to produce H_2 and CO (Zafar et.al., 2005). When the amount of oxygen brought by the metal oxide into the reduction reactor is below stoichiometric requirements, the chemical reaction with the fuel produces H_2 and CO. The reaction products may subsequently be shifted with steam to yield CO_2 and more H_2.

3.5.4.5 Use of decarbonised fuel in fuel cells

Fuel cells offer the possibility for highly efficient power production since the conversion process is not controlled by heat to work Carnot cycle restrictions (Blomen and Mugerwa, 1993). In general fuel cells feature the electrochemical oxidation of gaseous fuels directly into electricity, avoiding the mixture of the air and the fuel flows and thus the dilution with nitrogen and excess oxygen of the oxidised products (Campanari 2002). As a result, the anode outlet stream of a fuel cell has already a very high CO_2 content that simplifies the CO_2 capture sub system. The fuel is normally natural gas, though some concepts can also be incorporated into coal gasification systems. The systems concepts can be classified into two main groups (Goettlicher 1999):

- Systems with pre-fuel cell CO_2 capture
- Systems with post-fuel cell CO_2 capture.

In pre-fuel cell CO_2 capture systems (see Figure 3.18a) the fuel is first converted into hydrogen using steam reforming or coal gasification, followed by the water gas shift conversion. This system approach has been first proposed both for low temperature and for high temperature fuel cells.

Figure 3.18a. Fuel cell system with pre-fuel cell CO_2 capture.

The post-fuel cell capture system (see Figure 3.18b) is proposed for high temperature fuel cell systems (Dijkstra and Jansen, 2003). These systems make use of the internal reforming capabilities of the high temperature fuel cells resulting in an anode off-gas that has a high CO_2-content, but also contains H_2O and unconverted CO and H_2. The water can easily be removed by conventional techniques (cooling, knock-out, additional drying). Oxidising the H_2 and CO from the (SOFC) anode with air will result in a too high dilution of the stream with nitrogen. Haines (1999) chooses to use an oxygen-transport membrane reactor placed after the SOFC. The anode off-gas is fed to one side of the membrane, the cathode off-gas is fed to the other side of the membrane. The membrane is selective to oxygen, which permeates from the cathode off-gas stream to the anode off gas. In the membrane unit the H_2 and CO are oxidised. The retenate of the membrane unit consist of

CO_2 and water. Finally a concept using a water gas shift membrane reactor has been proposed (Jansen and Dijkstra, 2003).

Figure 3.18b. Fuel cell system with post fuel cell CO_2 capture.

3.5.5 Status and outlook

This section reviewed a wide variety of processes and fuel conversion routes that share a common objective: to produce a cleaner fuel stream from the conversion of a raw carbonaceous fuel into one that contains little, or none, of the carbon contained in the original fuel. This approach necessarily involves the separation of CO_2 at some point in the conversion process. The resulting H_2-rich fuel can be fed to a hydrogen consuming process, oxidised in a fuel cell, or burned in the combustion chamber of a gas turbine to produce electricity. In systems that operate at high pressure, the energy conversion efficiencies tend to be higher when compared to equivalent systems operating at low pressures following the combustion route, but these efficiency improvements are often obtained at the expense of a higher complexity and capital investment in process plants (see Section 3.7).

In principle, all pre-combustion systems are substantially similar in their conversion routes, allowing for differences that arise from the initial method employed for syngas production from gaseous, liquid or solid fuels and from the subsequent need to remove impurities that originate from the fuel feed to the plant. Once produced, the syngas is first cleaned, and then reacted with steam to produce more H_2 and CO_2. The separation of these two gases can be achieved with well-known, commercial absorption-desorption methods, producing a CO_2 stream suitable for storage. Also, intense R&D efforts worldwide are being directed to develop new systems that combine CO_2 separation with some of the reaction steps, such as the steam reforming of natural gas or water gas shift reaction stages, but it is not yet clear if these emerging concepts (see Section 3.5.3) will deliver a lower CO_2 capture cost.

In power systems, pre combustion CO_2 capture in natural gas combined cycles has not been demonstrated. However, studies show that based on current state of the art gas turbine combined cycles, pre-combustion CO_2 capture will reduce the efficiency from 56% LHV to 48% LHV (IEA 2000b). In natural gas combined cycles, the most significant area for efficiency improvement is the gas turbine and it is expected that by 2020, the efficiency of a natural gas combined cycle could be as high as 65% LHV (IEA GHG, 2000d). For such systems the efficiency with CO_2 capture would equal the current state of the art efficiency for plants without CO_2 capture, i.e., 56% LHV.

Integrated Gasification Combined Cycles (IGCC) are large scale, near commercial examples of power systems that can be implemented with heavy oil residues and solid fuels like coal and petroleum coke. For the embryonic coal-fired IGCC technology with the largest unit rated at 331 MW_e, future improvements are expected. A recent study describes improvements potentially realisable for bituminous coals by 2020 that could reduce both energy and cost-of-electricity penalties for CO_2 capture to 13% compared to a same base plant without capture. For such systems the generation efficiency with capture would equal the best efficiency realisable today without CO_2 capture (i.e. 43% LHV; IEA GHG, 2003). Notably, all the innovations considered, with the exception of ion transport membrane technology for air separation (which is motivated by many market drivers other than IGCC needs) involve, not “breakthrough” technologies, but rather modest continuing improvements in components that are already established commercially - improvements that might emerge as a natural result of growing commercial experience with IGCC technologies.

All fuel cell types are currently in the development phase. The first demonstration systems are now being tested, with the largest units being at the 1 MW scale. However, it will take at least another 5

to10 years before these units become commercially available. In the longer term, these highly efficient fuel cell systems are expected to become competitive for power generation. Integrating CO_2 capture in these systems is relatively simple and therefore fuel cell power generation systems offer the prospect of reducing the CO_2 capture penalty in terms of efficiency and capture costs. For instance, for high temperature fuel cell systems without CO_2 capture, efficiencies that exceed 67% are calculated with an anticipated 7% point efficiency reduction when CO_2 capture is integrated into the system (Jansen and Dijkstra, 2003). However, fuel cell systems are too small to reach a reasonable level of CO_2 transport cost (IEA GHG, 2002a), but in groups of a total of capacity 100MWe, the cost of CO_2 transport is reduced to a more acceptable level.

Most studies agree that pre-combustion systems may be better suited to implement CO_2 capture at a lower incremental cost compared to the same type of base technology without capture (Section 3.7), but with a key driver affecting implementation being the absolute cost of the carbon emission free product, or service provided. Pre-combustion systems also have a high strategic importance, because their capability to deliver, in a large scale and at high thermal efficiencies, a suitable mix of electricity, hydrogen and lower carbon containing fuels or chemical feed stocks in an increasingly carbon constrained world.

3.6 Environmental, monitoring, risk and legal aspects of capture systems

The previous sections of this chapter focused on each of the major technologies and systems for CO_2 capture. Here we summarize the major environmental, regulatory and risk issues associated with the use of CO_2 capture technology, and the handling of carbon dioxide common to all of these systems. Issues related to the subsequent transport and storage of carbon dioxide are discussed in Chapters 4 to 7.

3.6.1 Emissions and resource use impacts of CO_2 capture systems

3.6.1.1 Overview of emissions from capture systems

Plants with CO_2 capture would produce a stream of concentrated CO_2 for storage, plus in most cases a flue gas or vent gas emitted to the atmosphere and liquid wastes. In some cases solid wastes will also be produced.

The captured CO_2 stream may contain impurities which would have practical impacts on CO_2 transport and storage systems and also potential health, safety and environmental impacts. The types and concentrations of impurities depend on the type of capture process, as shown in Table 3.4, and detailed plant design. The major impurities in CO_2 are well known but there is little published information on the fate of any trace impurities in the feed gas such as heavy metals. If substances are captured along with the CO_2 then their net emissions to the atmosphere will be reduced, but impurities in the CO_2 may result in environmental impacts at the storage site.

Table 3.4. Concentrations of impurities in dried CO_2, vol % (Source data: IEA GHG 2003, IEA GHG 2004, IEA GHG 2005).

CO_2 from most capture processes contains moisture, which has to be removed to avoid corrosion and hydrate formation during transportation. This can be done using conventional processes and the costs of doing so are included in published costs of CO_2 capture plants.

CO_2 from post-combustion solvent scrubbing processes normally contains low concentrations of impurities. Many of the existing post-combustion capture plants produce high purity CO_2 for use in the food industry (IEA GHG 2004).

CO_2 from pre-combustion physical solvent scrubbing processes typically contains about 1-2% H_2 and CO and traces of H_2S and other sulphur compounds (IEA GHG 2003). IGCC plants with pre-combustion capture can be designed to produce a combined stream of CO_2 and sulphur compounds, to reduce costs and avoid the production of solid sulphur (IEA GHG, 2003). Combined streams of CO_2 and sulphur compounds (primarily hydrogen sulphide, H_2S) are already stored, for example in Canada, as discussed in Chapter 5. However, this option would only be considered in circumstances where the combined stream could be transported and stored in a safe and environmentally acceptable manner.

The CO_2-rich gas from oxy-fuel processes contains oxygen, nitrogen, argon, sulphur and nitrogen oxides and various other trace impurities. This gas will normally be compressed and fed to a cryogenic purification process to reduce the impurities concentrations to the levels required to avoid two-phase flow conditions in the transportation pipelines. 99.99% purity could be produced by including distillation in the cryogenic separation unit. Alternatively, the sulphur and nitrogen oxides could be left in the CO_2 fed to storage in circumstances where that is environmentally acceptable as described above for pre-combustion capture and when the total amount of all impurities left in the CO_2 is low enough to avoid two-phase flow conditions in transportation pipelines.

Power plants with CO_2 capture would emit a CO_2-depleted flue gas to the atmosphere. The concentrations of most harmful substances in the flue gas would be similar to or lower than in the flue gas from plants without CO_2 capture, because CO_2 capture processes inherently remove some impurities and some other impurities have to be removed upstream to enable the CO_2 capture process to operate effectively. For example, post-combustion solvent absorption processes require low concentrations of sulphur compounds in the feed gas to avoid excessive solvent loss, but the reduction in the concentration of an impurity may still result in a higher rate of emissions per kWh of product depending upon the actual amount removed upstream and the capture system energy requirements. As discussed below (Section 3.6.1.2), the latter measure is more relevant for environmental assessments. In the case of post combustion solvent capture, the flue gas may also contain traces of solvent and ammonia produced by decomposition of solvent.

Some CO_2 capture systems produce solid and liquid wastes. Solvent scrubbing processes produce degraded solvent wastes, which would be incinerated or disposed of by other means. Post-combustion capture processes produce substantially more degraded solvent than pre-combustion capture processes. However, use of novel post-combustion capture solvents can significantly reduce the quantity of waste compared to MEA solvent, as discussed in section 3.3.2.1. The waste from MEA scrubbing would normally be processed to remove metals and then incinerated. The waste can also be disposed of in cement kilns, where the waste metals become agglomerated in the clinker (IEA GHG 2004). Pre-combustion capture systems periodically produce spent shift and reforming catalysts which would be sent to specialist reprocessing and disposal facilities.

3.6.1.2 Framework for evaluating capture system impacts

As discussed in Chapter 1, the framework used throughout this report to assess the impacts of CO_2 capture and storage is based on the material and energy flows needed to produce a unit of product from a particular process. As seen earlier in this chapter, CO_2 capture systems require an increase in energy use for their operation. As defined in this report (see Section 1.5 and Figure 1.5.1), the energy requirement associated with CO_2 capture is expressed as the additional energy required to

produce a unit of useful product, such as a kilowatt-hour of electricity (for the case of a power plant). Because the energy and resource requirement for CO_2 capture (which includes the energy needed to compress CO_2 for subsequent transport and storage) is typically much larger than for other emission control systems, it has important implications for plant resource requirements and environmental emissions when viewed from the "systems" perspective of Figure 1.5.

In general, the CCS energy requirement per unit of product can be expressed in terms of the change in net plant efficiency (η) when the reference plant without capture is equipped with a CCS system:[1]

$$\Delta E = (\eta_{ref} / \eta_{ccs}) - 1 \quad (1)$$

where ΔE is the fractional increase in plant energy input per unit of product, and η_{ccs} and η_{ref} are the net efficiencies of the capture plant and reference plant, respectively. The CCS energy requirement directly determines the increases in plant-level resource consumption and environmental burdens associated with producing a unit of useful product (like electricity) while capturing CO_2. In the case of a power plant, the larger the CCS energy requirement, the greater are the increases per kilowatt-hour of in-plant fuel consumption and other resource requirements (such as water, chemicals and reagents), as well as environmental releases in the form of solid wastes, liquid wastes and air pollutants not captured by the CCS system. The magnitude of ΔE also determines the magnitude of additional upstream environmental impacts associated with the extraction, storage and transport of additional fuel and other resources consumed at the plant. However, the additional energy for these upstream activities is not normally included in the reported energy requirements for CO_2 capture systems.[2]

Recent literature on CO_2 capture systems applied to electric power plants quantifies the magnitude of CCS energy requirements for a range of proposed new plant designs with and without CO_2 capture. As elaborated later in Section 3.7 (Tables 3.7 to 3.15), those data reveal a wide range of ΔE values. For new supercritical pulverised coal (PC) plants using current technology, these ΔE values range from 24% to 40%, while for natural gas combined cycle (NGCC) systems the range is 11%–22%, and for coal-based gasification combined cycle (IGCC) systems it is 16%–25%. These ranges reflect the combined effects of the base plant efficiency and capture system energy requirements for the same plant type with and without capture.

3.6.1.3 Resource and emission impacts for current systems

Only recently have the environmental and resource implications of CCS energy requirements been discussed and quantified for a variety of current CCS systems. Table 3.5 displays the assumptions and results from a recent comparison of three common fossil fuel power plants employing current technology to capture 90% of the CO_2 produced (Rubin et al., 2005). Increases in specific fuel consumption relative to the reference plant without CO_2 capture correspond directly to the ΔE values defined above. For these three cases, the plant energy requirement per kWh increases by 31% for the PC plant, 16% for the coal-based IGCC plant, and 17% for the NGCC plant. For the

[1] A different measure of the "energy penalty" commonly reported in the literature is the fractional decrease in plant output (plant derating) for a fixed energy input. This value can be expressed as: $\Delta E^* = 1 - (\eta_{ccs}/\eta_{ref})$. Numerically, ΔE^* is smaller than the value of ΔE given by Equation (1). For example, a plant derating of $\Delta E^* = 25\%$ corresponds to an increase in energy input per kWh of $\Delta E = 33\%$.

[2] Those additional energy requirements, if quantified, could be included by re-defining the system boundary and system efficiency terms in Equation (1) to apply to the full life cycle, rather than only the power plant. Such an analysis would require additional assumptions about the methods of fuel extraction, processing, transport to the power plant, and the associated energy requirements of those activities; as well as the CO_2 losses incurred during storage.

specific examples used in Table 3.5, the increase in energy consumption for the PC and NGCC plants are in the mid-range of the values for these systems reported later in Tables 3.7 – 3.15 (see also Section 3.6.1.2), whereas the IGCC case is at the low end of the reported range for such systems As a result of the increased energy input per kWh of output, additional resource requirements for the PC plant include proportionally greater amounts of coal, as well as limestone (consumed by the FGD system for SO_2 control) and ammonia (consumed by the SCR system for NO_x control). All three plants additionally require more sorbent makeup for the CO_2 capture units. Table 3.5 also shows the resulting increases in solid residues for these three cases. In contrast, atmospheric emissions of CO_2 decrease sharply as a result of the CCS systems, which also remove residual amounts of other acid gases, especially SO_2 in flue gas streams. Thus, the coal combustion system shows a net reduction in SO_2 emission rate as a result of CO_2 capture. However, because of the reduction in plant efficiency, other air emission rates per kWh increase relative to the reference plants without capture. For the PC and NGCC systems, the increased emissions of ammonia are a result of chemical reactions in the amine-based capture process. Not included in this analysis are the incremental impacts of upstream operations such as mining, processing and transport of fuels and other resources. Other studies, however, indicate that these impacts, while not insignificant, tend to be small relative to plant-level impacts (Bock *et al.*, 2003).

Table 3.5. Illustrative impacts of CCS energy requirements on plant-level resource consumption and non- CO_2 emission rates for three current power plant systems.

For the most part, the magnitude of impacts noted above - especially impacts on fuel use and solid waste production - is directly proportional to the increased energy per kWh resulting from the reduction in plant efficiency, as indicated by Equation (3.6.1). Because CCS energy requirements are one to two orders of magnitude greater than for other power plant emission control technologies (such as particulate collectors and flue gas desulfurisation systems), the illustrative results above underscore the importance of maximizing overall plant efficiency while controlling environmental emissions.

3.6.1.4 Resource and emission impacts of future systems

The analysis above compared the impacts of CO_2 capture for a given plant type based on current technology. The magnitude of actual future impacts, however, will depend on four important factors: (1) the performance of technologies available at the time capture systems are deployed; (2) the type of power plants and capture systems actually put into service; (3) the total capacity of each plant type that is deployed; and, (4) the characteristics and capacity of plants they may be replacing.

Analyses of both current and near-future post-combustion, pre-combustion and oxy-fuel combustion capture technology options reveal that some of the advanced systems currently under development promise to significantly reduce the capture energy requirements—and associated impacts—while still reducing CO_2 emissions by 90% or more, as shown in Figure 3.19. Data in this figure was derived from the studies previously reported in Figures 3.6 and 3.7.

Figure 3.19. Fuel use for a reduction of CO_2 emissions from capture plants (data presented from design studies for power plants with and without capture shown in Figures 3.6 and 3.7).

The timetable for deploying more efficient plants with CO_2 capture will be the key determinant of actual environmental changes. If a new plant with capture replaces an older, less efficient and higher-emitting plant currently in service, the net change in plant-level emission impacts and resource requirements would be much smaller than the values given earlier (which compared identical new plants with and without capture). For example, the efficiency of a modern coal-based

plant with capture is close to many older coal-burning plants in service today. Replacing the latter with the former would thus reduce CO_2 emissions significantly with little or no net change in plant coal consumption or related solid waste impacts. In some cases, there could in fact be net reductions in other plant emissions, in support of clean air goals. If, however, the deployment of new CCS plants is delayed significantly, older existing plants could well be replaced by modern high-efficiency plants without capture. Such plants also would be built to provide additional capacity in regions with high electricity growth rates, such as in China and other parts of Asia today. A decade or two from now, the fleet of "existing" plants in those regions would thus look very different from the present. Accordingly, the environmental and resource impacts of additional new plants with CO_2 capture would have to be assessed in the context of the future situation.

Because comparisons of different plant types require a specific context (or scenario) to be meaningful, this chapter has only focused on characterizing the effects of CO_2 capture systems relative to the same type of power plant, and not the type of infrastructure it would replace (either currently, or in a future carbon-constrained world). If other systems such as the use of renewable energy, or electricity and synfuels co-generated from coal, find significant applications, those systems too would require more comprehensive comparative life-cycle assessments of resource use and impacts that are not currently available. Chapter 8, however, assesses overall energy use impacts for illustrative scenarios of CCS deployment in competition with other carbon mitigation options.

3.6.2 Issues related to the classification of carbon dioxide as a product

As a current commercial product, carbon dioxide is subject to classification and regulations. The classification of carbon dioxide is dependent on its physical state (gas, liquid or solid), its concentration, impurities present, and other criteria established by national legislative classification in different regions of the world. During the capture and concentration process, the quality properties can change the classification of the substance. For a detailed assessment of carbon dioxide physical and chemical properties, refer to the Appendix I.

The environmental, monitoring, risk and legal aspects associated with carbon dioxide handling and storage are well established in the processing industry. However, much larger volumes are targeted for carbon dioxide processing for purposes of CCS than the volumes handled at present. On a local and regional level, additional emergency response and other regulatory measures can be expected in the future depending on the rate of development of CCS. It is anticipated that human capacity will be developed to assess the monitoring, risk and legal aspects as required by the market.

At present, carbon dioxide typically occurs and is mainly traded as a non flammable gas (US Department of Transportation classification class 2.2). The classification system of Transport Dangerous Goods, International Maritime Organization/ International Maritime Dangerous Goods and International Civil Aviation Organization/ International Air Transport Association, all classify carbon dioxide in class 2.2 which are non-flammable, non corrosive and non-poisonous gases. In US federal regulations, carbon dioxide is not listed as a product in the Clean Water Act (CWA 307 and 311), Clean Air Act (CAA 112) or the Toxics Release Inventory. In other international regulations carbon dioxide is not classified in the European Inventory of Existing Commercial Chemical Substance or other international lists, but in Canada is classified as a compressed gas (class A), on the Canadian Energy Pipeline Association Dangerous Substances List as carbon dioxide (Hazardous Substances Data Bank, 2002). The physical-chemical properties of carbon dioxide are described in detail in Appendix I.

3.6.3 Health and safety risks associated with carbon dioxide processing

The effects of exposure to carbon dioxide are described in Appendix 1. However, a risk assessment that includes an understanding of both exposure and effects is required to characterize the risk for various situations associated with carbon dioxide processing (European Chemicals Bureau, 2003); see the following two sections for established risk management practices. The most probable routes of human exposure to carbon dioxide are inhalation or skin contact. The need for a risk based approach is clear from the following two descriptions. Carbon dioxide and its products of degradation are not legally classified as a toxic substance; is non-hazardous on inhalation, is a non-irritant and does not sensitise or permeate the skin. However, chronic effects on humans follow from long term exposure to airborne carbon dioxide concentrations between 0.5 and 1%, result in metabolic acidosis and increased calcium deposits in soft tissues. The substance is toxic to the cardiovascular system and upper respiratory tract at concentrations above 3%. Sensitive populations to elevated carbon dioxide levels are described in Appendix 1. The product risk assessment process is therefore necessary as with any other chemical use to determine the risk and establish the necessary risk management processes.

As an asphyxiate carbon dioxide presents the greatest danger. If atmospheric oxygen is displaced such that oxygen concentration is 15 to 16% signs of asphyxia will be noted. Skin contact with dry ice has caused serious frostbites and blisters (Hazardous Substances Data Bank, 2002). Protective equipment and clothing required in the processing industries include full face-piece respirators to prevent eye contact and appropriate personal protective clothing to protect the skin from becoming frozen by the liquid.

3.6.4 Plant design principles and guidelines used by governments, industries and financiers

New plant facilities like those envisioned for carbon dioxide are subject to design guidelines for the petrochemical industry as determined by relevant authorities. One example is the European Unions' Integrated Pollution Prevention and Control (IPPC) directive requiring the application of the principles of Best Available Technology Not Entailing Excessive Cost (BATNEEC). Carbon dioxide capture and compression processes are listed in several guidelines as gas processing facilities. Typically the World Bank guidelines and other financial institutions have specific requirements to reduce risk and require monitoring (World Bank, 1999) which is part of routine plant monitoring to detect accidental releases. Investor guidelines like the World Bank guidelines are particularly important for developing countries where there is less emphasis on monitoring and legislation. National and regional legislation for plant design and specifications from organizations like the US Environmental Protection Agency are available to guide the development of technology.

3.6.5 Commissioning, good practice during operations and sound management of chemicals

The routine engineering design, commissioning and start-up activities associated with petrochemical facilities are applicable to the capture and compression of carbon dioxide; for example Hazard Operability studies are conducted on a routine basis for new facilities (Sikdar and Diwekar, 1999).

The management of carbon dioxide and reagents inside factory battery limits will be in accordance with the relevant practices in use for carbon dioxide. For carbon dioxide, US Occupational Health and Safety Act standards and National Institute for Occupational Safety and Health recommendations exist which are applied widely in industry to guide safe handling of carbon dioxide, and the same applies to reagents and catalysts used. Well established and externally audited management systems such as International Standards Organization's ISO 14001 (environment) and ISO 9001 (quality), and Occupational Health and Safety (OHSAS 18000) exist

to provide assurance that environment, safety, health and quality management systems are in place (American Institute of Chemical Engineers, 1995). Tools like life cycle assessment (ISO 14040 series) with the necessary boundary expansion methodology are useful to determine the overall issues associated with a facility and assist with selection of parameters such as energy carriers, operational conditions and materials used in the process. The life cycle assessment will also indicate if a trouble free capture system does generate environmental concerns elsewhere in the product life cycle.

3.6.6 Site closure and remediation

It is not anticipated that carbon dioxide capture will result in a legacy of polluted sites requiring remediation after plant closure, assuming that standard operating procedures and management practices in the previous section are followed. However, depending on the technology used and the materials procured for operations, waste disposal at the facilities and operation according to a formal management system from construction, operation to the development of site closure plans will largely assist to reduce the risk of a polluted site after closure of operations.

3.7 Cost of CO_2 capture

This section of the report deals with the critical issue of CO_2 capture costs. We begin with an overview of the many factors that affect costs and the ability to compare published estimates on a consistent basis. Different measures of CO_2 capture cost also are presented and discussed. The literature on CO_2 capture costs for currently available technologies is then reviewed, along with the outlook for future costs over the next several decades.

3.7.1 Factors affecting CO_2 capture cost

Published estimates for CO_2 capture costs vary widely, mainly as a result of different assumptions regarding technical factors related to plant design and operation (e.g., plant size, net efficiency, fuel properties and load factor), as well as key economic and financial factors such as fuel cost, interest rates and plant lifetime. A number of recent papers have addressed this issue and identified the principal sources of cost differences and variability (Herzog, 1999; Simbeck, 1999; Rubin and Rao, 2003). This section draws heavily on Rubin and Rao (2003) to highlight the major factors affecting the cost of CO_2 capture.

3.7.1.1 Defining the Technology of Interest

Costs will vary with the choice of CO_2 capture technology and the choice of power system or industrial process that generates the CO_2 emissions. In engineering-economic studies of a single plant or CO_2 capture technology, such definitions usually are clear. However, where larger systems are being analyzed, such as in regional, national or global studies of CO_2 mitigation options, the specific technologies assumed for CO_2 production and capture may be unclear or unspecified. In such cases, the context for reported cost results also may be unclear.

3.7.1.2 Defining the System Boundary

Any economic assessment should clearly define the "system" whose CO_2 emissions and cost is being characterized. The most common assumption in studies of CO_2 capture is a single facility (most often a power plant) that captures CO_2 and transports it to an off-site storage area such as a geologic formation. The CO_2 emissions considered are those released at the facility before and after capture. Reported costs may or may not include CO_2 transport and storage costs. *The system boundary of interest in this section of the report includes only the power plant or other process of interest, and does not include CO_2 transport and storage systems, whose costs are presented in*

later chapters. CO_2 compression, however, is assumed to occur within the facility boundary, and therefore the cost of compression is included in the cost of capture.[3]

In some studies the system boundary includes emissions of CO_2 and other greenhouse gases such as methane (expressed as equivalent CO_2) over the complete fuel cycle encompassing not only the power plant or facility in question, but also the "upstream" processes of extraction, refining and transport of fuel used at the facility, plus any "downstream" emissions from the use or storage of captured CO_2. Still larger system boundaries might include all power plants in a utility company's system; all plants in a regional or national grid; or a national economy where power plant and industrial emissions are but one element of the overall energy system being modeled. In each of these cases it is possible to derive a mitigation cost for CO_2, but the results are not directly comparable because they reflect different system boundaries and considerations. Chapter 8 discusses such differences in more detail and presents results for alternative systems of interest.

3.7.1.3 Defining the Technology Time Frame and Maturity

Another factor that is often unclear in economic evaluations of CO_2 capture is the assumed time frame and/or level of maturity for the technology under study. Does the cost estimate apply to a facility that would be built today, or at some future time? This is especially problematic in studies of "advanced" technologies that are still under development and not currently commercial. In most cases, studies of advanced technologies assume that costs apply to an "n^{th} plant" to be built sometime in the future when the technology is mature. Such estimates reflect the expected benefits of technological learning, but may or may not adequately account for the increased costs that typically occur in the early stages of commercialization. The choice of technology time frame and assumed rate of cost improvements thus can make a big difference in CO_2 capture cost estimates.

3.7.1.4 Different Cost Measures and Assumptions

The literature reveals a number of different measures used to characterize CO_2 capture and storage costs, including capital cost, cost of electricity, cost of CO_2 avoided, and others. Because some of these measures are reported in the same units (e.g., dollars per tonne of CO_2) there is great potential for misunderstanding. Furthermore, for any given cost measure, different assumptions about the technical, economic and financial parameters used in cost calculations also can give rise to large differences in reported capture costs. Section 3.7.2 elaborates on some of the common metrics of cost and the parameters they employ.

3.7.2 Measures of CO_2 capture cost

We define here four common measures of CO_2 capture cost: capital cost, incremental product cost (such as the cost of electricity), cost of CO_2 avoided, and cost of CO_2 captured or removed. Each of these measures provides a different perspective on CO_2 capture cost for a particular technology or system of interest. All of them, however, represent an "engineering economic" perspective showing the added cost of capturing CO_2 in a particular application. Such measures are required to address larger questions such as which options or strategies to pursue—a topic addressed later in Chapter 8.

3.7.2.1 Capital Cost

Capital cost (also known as investment cost or first cost) is a widely used, albeit incomplete, metric of the cost of a technology. Often it is reported on a normalized basis (e.g., cost per kW). For CO_2

[3] Alternatively, compression costs could be attributed wholly or in part to CO_2 transport and storage. Most studies, however, include compression with capture cost. This also facilitates comparisons of capture technologies that operate at different pressures, and thus incur different costs to achieve a specified final pressure.

capture systems, the capital cost is generally assumed to represent the total expenditure required to design, purchase and install the system of interest. It may also include the additional costs of other plant components not needed in the absence of a CO_2 capture device, such as the costs of an upstream gas purification system to protect the capture device. Such costs often arise in complex facilities like a power plant. Thus, the total incremental cost of CO_2 capture for a given plant design is best determined as the difference in total cost between plants with and without CO_2 capture, producing the same amounts of useful (primary) product, such as electricity.

Different organizations employ different systems of accounts to specify the elements of a capital cost estimate. For electric power plants, one widely used procedure is that defined by the Electric Power Research Institute (EPRI) (EPRI, 1993). However, because there is no universally employed nomenclature or system of accounts, capital costs reported by different organizations or authors may not always include the same items. The terms used to report capital costs may further disguise such differences and lead to misunderstandings about what is and is not included. For example, power plant cost studies often report a value of capital cost that does not include the cost of interest during construction or other so-called "owners costs" that typically add at least 10% to 20% (sometimes substantially more) to the "total capital requirement" of a system. Only if a capital cost breakdown is reported can such omissions be discovered. Studies that fail to report the year of a cost estimate introduce further uncertainty that may affect cost comparisons.

3.7.2.2 Incremental Product Cost

The effect of CO_2 capture on the cost of electricity (or other product) is one of the most important measures of economic impact. Electric power plants, a major source of CO_2 emissions, are of particular interest in this regard. The cost electricity (COE) for a power plant can be calculated as:[4]

$$COE = [(TCR)(FCF) + (FOM)]/[(CF)(8760)(kW)] + VOM + (HR)(FC) \quad (1)$$

where, COE = levelized cost of electricity (US$/kWh), TCR = total capital requirement (US$), FCF = fixed charge factor (fraction/yr), FOM = fixed operating costs (US$/yr), VOM = variable operating costs (US$/kWh), HR = net plant heat rate (kJ/kWh), FC = unit fuel cost (US$/kJ), CF = capacity factor (fraction), 8760 = total hours in a typical year, and kW = net plant power (kW). In this chapter, the costs in Equation (1) include only the power plant and capture technologies, and not the additional costs of CO_2 transport and storage that are required for a complete system with CCS. The incremental COE is the difference in electricity cost with and without CO_2 capture.[5] Again, the values reported here exclude transport and storage costs. Full CCS costs are reported in Chapter 8.

Eq. (1) shows that many factors affect this incremental cost. For example, just as the total capital cost includes many different items, so too do the fixed and variable costs associated with plant operation and maintenance (O&M). Similarly, the fixed charge factor (FCF, also known as the capital recovery factor) reflects assumptions about the plant lifetime and the effective interest rate

[4] For simplicity, the value of FCF in Eq.(1) is applied to the total capital requirement. More detailed calculations of COE based on a year-by-year analysis apply the FCF to the total capital cost excluding owner's costs (such as interest during construction), which are separately accounted for in the years prior to plant start up.

[5] For CO_2 capture systems with large auxiliary energy requirements, the magnitude of incremental cost also depends on whether the plant with capture is assumed to be a larger facility producing the same net output as the reference plant without capture, or whether the reference plant is simply derated to supply the auxiliary energy. While the latter assumption is most common, the former yields a smaller incremental cost due to economy-of-scale effects.

(or discount rate) used to amortize capital costs.[6] Assumptions about any of the factors in Eq. (1) can have a pronounced effect on overall cost results. Nor are these factors all independent of one another. For example, the design heat rate of a new power plant may affect the total capital requirement since high-efficiency plants usually are more costly than lower-efficiency designs.

Finally, because several of the parameter values in Eq. (1) may change over the operating life of a facility (such as the capacity factor, unit fuel cost, or variable operating costs), the value of COE also may vary from year to year. To include such effects, an economic evaluation would calculate the net present value (NPV) of discounted costs based on a schedule of year-to-year cost variations, in lieu of the simpler formulation of Eq. (1). However, most engineering-economic studies use Eq. (1) to calculate a single value of "levelized" COE over the assumed life of the plant. The levelized COE is the cost of electricity, which, if sustained over the operating life of the plant, would produce the same NPV as an assumed stream of variable year-to-year costs. In most economic studies of CO_2 capture, however, all parameter values in Eq. (1) are held constant, reflecting (either implicitly or explicitly) a levelized COE over the life of the plant.[7]

3.7.2.3 Cost of CO_2 Avoided

One of the most widely used measures for the cost of CO_2 capture and storage is the "cost of CO_2 avoided." This value reflects the average cost of reducing atmospheric CO_2 mass emissions by one unit while providing the same amount of useful product as a "reference plant" without CCS. For an electric power plant the avoidance cost can be defined as:

$$\text{Cost of } CO_2 \text{ Avoided (US\$/tonne } CO_2) = [(COE)_{capture} - (COE)_{ref}] / [(CO_2/kWh)_{ref} - (CO_2/kWh)_{capture}] \quad (2)$$

where, COE = levelized cost of electricity (US$/kWh) as given by Eq. (1), and CO_2/kWh = CO_2 mass emission rate (in tonnes) per kWh generated, based on the net plant capacity for each case. The subscripts "capture" and "ref" refer to the plant with and without CO_2 capture, respectively. Note that while this equation is commonly used to report a cost of CO_2 avoided for the capture portion of a full CCS system, strictly speaking it should be applied only to a complete CCS system including transport and storage costs (since all elements are required to avoid emissions to the atmosphere).

The choice of the reference plant without CO_2 capture plays a key role in determining the CO_2 avoidance cost. *Here the reference plant is assumed to be a plant of the same type and design as the plant with CO_2 capture.* This provides a consistent basis for reporting the incremental cost of CO_2 capture for a particular type of facility.

Using Equation (2), a cost of CO_2 avoided can be calculated for any two plant types, or any two aggregates of plants. Thus, special care should be taken to ensure that the basis for a reported cost of CO_2 avoided is clearly understood or conveyed. For example, the avoidance cost is sometimes taken as a measure of the cost to society of reducing GHG emissions.[8] In that case, the cost per tonne of CO_2 avoided reflects the average cost of moving from one situation (e.g., the current mix

[6] In its simplest form, FCF can be calculated from the project lifetime, n (years), and annual interest rate, i (fraction), by the equation: $FCF = i / [1 - (1 + i)^{-n}]$.

[7] Readers not familiar with these economic concepts and calculations may wish to consult a basic economics text, or references such as (EPRI, 1993) or (Rubin, 2001) for more details.

[8] As used here, "cost" refers only to money spent for technology, fuels and related materials, and not to broader societal measures such as macroeconomic costs or societal damage costs associated with atmospheric emissions. Further discussions and use of the term "cost of CO_2 avoided" appear in Chapter 8 and in the references cited earlier.

of power generation fuels and technologies) to a different mix of technologies having lower overall emissions. Alternatively, some studies compare individual plants with and without capture (as we do), but assume different types of plants for the two cases. Such studies, for example, might compare a coal-fired plant with capture to an NGCC reference plant without capture. Such cases reflect a different choice of system boundaries, and address very different questions, than those addressed here. However, the data presented in this section (comparing the same type of plant with and without capture) can be used to estimate a cost of CO_2 avoided for any two of the systems of interest in a particular situation (see Chapter 8).

3.7.2.4 Cost of CO_2 Captured or Removed

Another cost measure frequently reported in the literature is based on the mass of CO_2 captured (or removed) rather than emissions avoided. For an electric power plant it can be defined as:

$$\text{Cost of } CO_2 \text{ Captured (US\$/tonne } CO_2) = [(COE)_{capture} - (COE)_{ref}] / (CO_{2,\,captured}/kWh) \quad (3)$$

where, $CO_{2,\,captured}/kWh$ = total mass of CO_2 captured (in tonnes) per net kWh for the plant with capture. This measure reflects the economic viability of a CO_2 capture system given a market price for CO_2 (as an industrial commodity). If the CO_2 captured at a power plant can be sold at this price (e.g., to the food industry, or for enhanced oil recovery), the COE for the plant with capture would be the same as for the reference plant having higher CO_2 emissions. Numerically, the cost of CO_2 captured is lower than the cost of CO_2 avoided because the energy required to operate the CO_2 capture systems increases the amount of CO_2 emitted per unit of product.

3.7.2.5 Importance of CCS Energy Requirements

Because the energy requirement for CCS is substantially larger than for other emission control systems, it has important implications for plant economics as well as for resource requirements and environmental impacts. The energy "penalty" (as it is often called) enters cost calculations in one of two ways. Most commonly, all energy needed to operate CCS absorbers, compressors, pumps, and other equipment is assumed to be provided within the plant boundary, thus lowering the net plant capacity (kW) and output (kWh, in the case of a power plant). The result, as shown by Eq.(1), is a higher unit capital cost (US$/kW) and a higher cost of electricity production (US$/kWh). Effectively, these higher unit costs reflect the expense of building and operating the incremental capacity needed to operate the CCS system.

Alternatively, some studies—particularly for industrial processes such as hydrogen production—assume that some or all of the energy needed to operate the CCS system is purchased from outside the plant boundary at some assumed price. Still other studies assume that new equipment is installed to generate auxiliary energy on-site. In these cases, the net plant capacity and output may or may not change, and may even increase. However, the COE in Eq.(1) again will rise due to the increases in VOM costs (for purchased energy) and (if applicable) capital costs for additional equipment. The assumption of purchased power, however, does not guarantee a full accounting of the replacement costs or CO_2 emissions associated with CCS. In all cases, however, the larger the CCS energy requirement, the greater the difference between the costs of CO_2 captured and avoided.

3.7.2.6 Other Measures of Cost

The cost measures above characterize the expense of adding CO_2 capture to a single plant of a given type and operating profile. A broader modeling framework is needed to address questions involving multiple plants (e.g., a utility system, regional grid, or national network), or decisions about what type of plant to build (and when). Macroeconomic models that include emission control

costs as elements of a more complex framework typically yield cost measures such as the change in gross domestic product (GDP) from the imposition of a carbon constraint, along with changes in the average cost of electricity and cost per tonne of CO_2 abated. Such measures are often useful for policy analysis, but reflect many additional assumptions about the structure of an economy as well as the cost of technology. Chapter 8 provides a discussion of macroeconomic modeling as it relates to CO_2 capture costs.

3.7.3 The context for current cost estimates

Recall that CO_2 capture, while practiced today in some industrial applications, is not currently a commercial technology used at large electric power plants, which are the focus of most CCS studies. Thus, cost estimates for CO_2 capture systems rely mainly on studies of hypothetical plants. Published studies also differ significantly in the assumptions used for cost estimation. Equation (1), for example, shows that the plant capacity factor has a major impact on the cost of electric power generation, as do the plant lifetime and discount rate used to compute the fixed charge factor. The COE, in turn, is a key element of CO_2 avoidance cost, Eq. (2). Thus, a high plant capacity factor or a low fixed charge rate will lower the cost of CO_2 capture per kWh. The choice of other important parameters, such as the plant size, efficiency, fuel type and CO_2 removal rate will similarly affect the CO_2 capture cost. Less apparent, but often equally important, are assumptions about parameters such as the "contingency cost factors" embedded in capital cost estimates to account for unspecified costs anticipated for technologies at an early stage of development, or for commercial systems that have not yet been demonstrated for the application, location, or plant scale under study.

Because of the variability of assumptions employed in different studies of CO_2 capture, a systematic comparison of cost results is not straightforward (or even possible in most cases). Moreover, there is no universally "correct" set of assumptions that apply to all the parameters affecting CO_2 capture cost. For example, the quality and cost of natural gas or coal delivered to power plants in Europe and the United States may differ markedly. Similarly, the cost of capital for a municipal or government-owed utility may be significantly lower than for a privately-owned utility operating in a competitive market. These and other factors lead to real difference in CO_2 capture costs for a given technology or power generation system. Thus, we seek in this report to elucidate the key assumptions employed in different studies of similar systems and technologies, and their resulting impact on the cost of CO_2 capture. Analyses comparing the costs of alternative systems on an internally consistent basis (within a particular study) also are highlighted. Nor are all studies equally credible, considering their vintage, data sources, level of detail, and extent of peer review. Thus, the approach adopted here is to rely as much as possible on recent peer-reviewed literature, together with other publicly-available studies by governmental and private organizations heavily involved in the field of CO_2 capture. Later, in Chapter 8, the range of capture costs reported here are combined with cost estimates for CO_2 transport and storage to arrive at estimates of the overall cost of CCS for selected power systems and industrial processes.

3.7.4 Overview of technologies and systems evaluated

Economic studies of CO_2 capture have focused mainly on electric power generation, a major source of CO_2 emissions. To a lesser extent, CO_2 capture from industrial processes also has been subject to economic evaluations, especially processes producing hydrogen, often in combination with other products.

The sections below review and summarize recent estimates of CO_2 capture costs for major systems of interest. Sections 3.7.4 to 3.7.7 focus first on the cost of current CO_2 capture technologies, while Sections 3.7.8 to 3.7.11 go on to discuss improved or "advanced" technologies promising lower costs in the future. In all cases the system boundary is defined as a single facility at which CO_2 is

captured and compressed for delivery to a transport and storage system. To reflect different levels of confidence (or uncertainty) in cost estimates for technologies at different stages of development, the qualitative descriptors shown in Table 3.6 are applied in summarizing published cost estimates.[9] The studies reviewed typically report costs in U.S. dollars for reference years ranging from 2000 to early 2004. Because inflation effects generally have been small during this period no adjustments have been made in summarizing ranges of reported costs.

Table 3.6. Confidence levels for technology and system cost estimates.

3.7.5 Post-combustion CO_2 capture cost for electric power plants (current technology)

Most of the world's electricity is currently generated from the combustion of fossil fuels, especially coal and (to an increasing extent) natural gas. Hence, the ability to capture and sequester the CO_2 emitted by such plants has been a major focus of investigation. This section of the report focuses on the cost of currently available technology for CO_2 capture. Because of the relatively low CO_2 concentration in power plant flue gases, chemical absorption systems have been the dominant technology of interest for post-combustion capture (see Section 3.3.2). However, the cost of CO_2 capture depends not only on the choice of capture technology, but also—and often more importantly - on the characteristics and design of the overall power plant. For purposes of cost reporting, we distinguish between coal-fired and gas-fired plant designs, and between new and existing facilities.

3.7.5.1 New Coal-Fired Power Plants

Table 3.7 summarizes the key assumptions and results of recent studies of post-combustion CO_2 capture at new coal-fired power plants. Assumed plant sizes with CO_2 capture range from approximately 300-700 MW net power output. In all cases, CO_2 capture is accomplished using an amine-based absorption system, typically MEA. Capture efficiencies range from 85% to 95% with the most common value being 90%. The studies employ different assumptions about other key parameters such as the base power plant efficiency, coal properties, coal cost, plant capacity factor, CO_2 product pressure, and financial parameters such as the fixed charge factor. All of these factors have a direct influence on total plant cost and the cost of CO_2 capture.

Table 3.7. CO_2 Capture Costs: New Coal-Fired Power Plants with Current Capture Technology.

Table 3.7 summarizes several measures of CO_2 capture cost, both in absolute and relative terms. Across the full set of studies, CO_2 capture adds 44-87% to the capital cost of the reference plant (US$/kW) and 42-81% to the cost of electricity (US$/MWh), while achieving CO_2 reductions of approximately 80-90% per net kWh produced. The cost of CO_2 avoided for these cases varies from 29-51 US$/tonne CO_2. The absolute values of capital cost, COE, and incremental cost of electricity in Table 3.7 reflect the different assumptions employed in each study. The result is an incremental COE of 18-38 US$/MWh (or 1.8 to 3.8 c/kWh) for CO_2 capture. The total COE for plants with capture ranges from 62-87 US$/MWh. In all cases, a significant portion of the total CO_2 capture cost is due to the energy requirement for CO_2 capture and compression. For the studies in Table 3.7, the plants with CO_2 capture require 24% to 42% more fuel input per MWh of plant output relative to a similar reference plant without capture. Roughly half the energy is required for solvent regeneration and a third for CO_2 compression.

[9] These descriptions are used in subsequent tables to characterize systems with CO_2 capture. In most cases the cost estimates for reference plants (without capture) would rank as high (e.g., IGCC power plants) or very high (e.g., PC and NGCC power plants).

While many factors contribute to the cost differences observed in Table 3.7, systematic studies of the influence of different factors indicate that the most important sources of variability in reported cost results are assumptions about the CO_2 capture system energy requirement, power plant efficiency, fuel type, plant capacity factor and fixed charge rate (Rao and Rubin, 2002). In this regard, it is useful to note that the lowest-cost capture systems in Table 3.7 (in terms of COE and cost of CO_2 avoided) come from a recent study (IEA GHG, 2004) that combines an efficient supercritical power plant design using bituminous coal, with high plant utilization, lowest fixed charge rate, and more energy-efficient amine system designs, as recently announced by two major vendors (but not yet demonstrated on coal-fired power plants). In contrast, the highest reported COE values are for less efficient subcritical plant designs using low rank coal, combined with lower capacity factors, higher fixed charge rates, and employing amine system designs typical of units currently in operation at small power plants.

Recent increases in world coal prices, if sustained, also would affect the levelized COE values reported here. Based on one recent study (IEA GHG, 2004), each 1.00 US$/GJ increase in coal price would increase the COE by 8.2 US$/MWh for a new PC plant without capture, and by 10.1 US$/MWh for a plant with capture.

These results indicate that new power plants equipped with CO_2 capture are likely to be high-efficiency supercritical units, which yield lowest overall costs. The worldwide use of supercritical units (without capture) with current usage at 155 GWe (Section 3.1.2.2), is rapidly increasing in several regions of the world and, as seen in Table 3.7, the preponderance of recent studies of CO_2 capture are based on supercritical units using bituminous coals. For these plants, Table 3.7 shows that capture systems increase the capital cost by 44-74%, and the COE by 42-66% (18-34 US$/MWh). The major factors contributing to these ranges were differences in plant size, capacity factor and fixed charge factor. New or improved capture systems and power plant designs that promise to further reduce the costs of CO_2 capture are discussed later in Section 3.7.7. First, however, we examine CO_2 capture costs at existing plants.

3.7.5.2 Existing Coal-Fired Plants

Compared to the study of new plants, CO_2 capture options for existing power plants has received relatively little study to date. Table 3.8 summarizes the assumptions and results of several studies estimating the cost of retrofitting an amine-based CO_2 capture system to an existing coal-fired power plant. Several factors significantly affect the economics of retrofits, especially the age, smaller sizes, and lower efficiencies typical of existing plants relative to new builds. The energy requirement for CO_2 capture also is usually higher because of less efficient heat integration for sorbent regeneration. All of these factors lead to higher overall costs. Existing plants not yet equipped with a flue gas desulfurization (FGD) system for SO_2 control also must be retrofitted or upgraded for high-efficiency sulfur capture in addition to the CO_2 capture device. For plants with high NO_x levels, a NO_2 removal system also may be required to minimize solvent loss from reactions with acid gases. Finally, site-specific difficulties, such as land availability, access to plant areas and need for special ductwork, tend to further increase the capital cost of any retrofit project relative to an equivalent new plant installation. Nonetheless, in cases where the capital cost of the existing plant has been fully or substantially amortized, Table 3.8 shows that the COE of a retrofitted plant with capture (including all new capital requirements) can be comparable to or lower than that of a new plant, although the incremental COE is typically higher because of the factors noted above.

Table 3.8. CO_2 Capture Costs: Existing Coal-Fired Power Plants with Current Capture Technology.

Table 3.8 further shows that for comparable levels of about 85% CO_2 reduction per kWh, the average cost of CO_2 avoided for retrofits is about 35% higher than for the new plants analyzed in Table 3.7. The incremental capital cost and COE depend strongly on site-specific assumptions, including the degree of amortization and options for providing process energy needs. As with new plants, heat and power for CO_2 capture are usually assumed to be provided by the base (reference) plant, resulting in a sizeable (30 to 40%) plant output reduction. Other studies assume that an auxiliary gas-fired boiler is constructed to provide the CO_2 capture steam requirements and (in some cases) additional power. Low natural gas prices can make this option more attractive than plant output reduction (based on COE), but such systems yield lower CO_2 reductions (around 60%) since the emissions from natural gas combustion typically are not captured. For this reason, the avoided cost values for this option are not directly comparable to those with higher CO_2 reductions.

Also reflected in Table 3.8 is the option of rebuilding an existing boiler and steam turbine as a supercritical unit to gain efficiency improvements in conjunction with CO_2 capture. One recent study (Gibbins, et.al, 2005) suggests this option could be economically attractive in conjunction with CO_2 capture since the more efficient unit minimizes the cost of capture and yields a greater net power output and a lower COE compared to a simple retrofit. The use of a new and less energy-intensive capture unit yields further cost reductions in this study. Another recent study similarly concluded that the most economical approach to CO_2 capture for an existing coal-fired plant was to combine CO_2 capture with repowering the unit with an ultrasupercritical steam system (Simbeck, 2004). One additional option, repowering an existing unit with a coal gasifier, is discussed later in Section 3.7.5.2.

3.7.5.3 Natural Gas-Fired Power Plants

Power plants fuelled by natural gas may include gas-fired boilers, simple-cycle gas turbines, or natural gas combined cycle (NGCC) units. The current operating capacity in use globally is 333 GWe for gas-fired boilers, 214 GWe for simple cycle gas turbines and 339 GWe for NGCC (IEA WEO, 2004).The absence of sulfur and other impurities in natural gas reduces the capital costs associated with auxiliary flue gas cleanup systems required for amine-based CO_2 capture technology. On the other hand, the lower concentration of CO_2 in gas-fired units tends to increase the cost per tonne of CO_2 captured or avoided relative to coal-fired units.

Table 3.9. CO_2 Capture Costs: Natural Gas-Fired Power Plants with Current Capture Technology.

Table 3.9 summarizes the assumptions and cost results of several recent studies of CO_2 capture at gas-fired combined cycle power plants ranging in size from approximately 300 to 700 MW. Relative to reference plants without capture, to achieve net CO_2 reductions (per kWh) of the order of 83-88%, the capital cost per kW increases by 64-100%, while the COE increases by 37-69%, or by 12-24 US$/MWh on an absolute basis. The corresponding cost of CO_2 avoided ranges from 37-74 US$/tonne CO_2, while the CCS energy requirement increases plant fuel consumption per kWh by 11-22%.

As seen earlier in Equations (1) – (3), assumptions about the plant fuel cost have an especially important influence on the COE for gas-fired plants because the contribution of capital costs is relatively low compared to coal plants. The studies in Table 3.9 assume stable gas prices of 2.82-4.44 US$/GJ (LHV basis) over the life of the plant, together with high capacity factors (65-95%) representing base load operation. These assumptions result in relatively low values of COE for both the reference plant and capture plant. Since about 2002, however, natural gas prices have increased significantly in many parts of the world, which has also affected the outlook for future prices. Based

on the assumptions of one recent study (IEA GHG, 2004), the COE for an NGCC plant without capture would increase by 6.8 US$/MWh for each 1.00 US$/GJ increase in natural gas price (assuming no change in plant utilization or other factors of production). An NGCC plant with CCS would see a slightly higher increase of 7.3 US$/MWh. The price of natural gas, and its relation to the price of competing fuels like coal, is an important determinant of which type of power plant will provide the lowest cost electricity in the context of a particular situation. However, across a twofold increase in gas price (from 3-6 US$/GJ), the incremental cost of CO_2 capture changed by only 2 US$/MWh (0.2 c/kWh) with all other factors held constant.

In countries like the U.S., higher gas prices also have resulted in lower utilization rates (averaging 30-50%) for plants originally designed for base load operation, but where lower-cost coal plants are available for dispatch. This further raises the average cost of electricity and CO_2 capture for those NGCC plants, as reflected in one case in Table 3.9 with a capacity factor of 50%. In other parts of the world, however, lower-cost coal plants may not be available, or gas supply contracts might limit the ability to curtail gas use. Such situations again illustrate that options for power generation with or without CO_2 capture should be evaluated in the context of a particular situation or scenario.

Studies of commercial post-combustion CO_2 capture applied to simple-cycle gas turbines have been conducted for the special case of retrofitting an auxiliary power generator in a remote location (CCP, 2005). This study reported a relatively high cost of 88 US$/tonne CO_2 avoided. Studies of post-combustion capture for gas-fired boilers have been limited to industrial applications, as discussed later in Section 3.7.8.

3.7.5.4 Biomass-firing and Co-firing Systems

Power plants can be designed to be fueled solely by biomass, or biomass can be co-fired in conventional coal-burning plants. The requirement to reduce net CO_2 emissions could lead to an increased use of biomass fuel, because plants that utilize biomass as a primary or supplemental fuel may be able to take credit for the carbon removed from the atmosphere during the biomass growth cycle. If the biomass carbon released during combustion (as CO_2) is then captured and sequestered, the net quantity of CO_2 emitted to the atmosphere could in principle be negative.

The most important factor affecting the economics of biomass use is the cost of the biomass. This can range from a negative value, as in the case of some biomass wastes, to costs substantially higher than coal, as in the case of some purposely-grown biomass fuels, or wastes that have to be collected from diffuse sources. Power plants that use only biomass are typically smaller than coal-fired plants because local availability of biomass is often limited, and biomass is more bulky and hence more expensive to transport than coal. The smaller sizes of biomass-fired plants would normally result in lower energy efficiencies and higher costs of CO_2 capture. Biomass can be co-fired with coal in larger plants (Robinson et.al, 2003). In such circumstances the incremental costs of capturing biomass-derived CO_2 should be similar to costs of capturing coal-derived CO_2. Another option is to convert biomass into pellets or refined liquid fuels to reduce the cost of transporting it over long distances. However, there are costs and emissions associated with production of these refined fuels. Information on costs of CO_2 capture at biomass-fired plants is sparse but some information is given in Section 3.7.8.4. The overall economics of CCS with biomass combustion will depend very much on local circumstances, especially biomass availability and cost and (as with fossil fuels) proximity to potential CO_2 storage sites.

3.7.6 Pre-combustion CO_2 capture cost for electric power plants (current technology)

Studies of pre-combustion capture for electric power plants have focused mainly on integrated gasification combined cycle (IGCC) systems using coal or other solid fuels such as petroleum coke.

This section of the report focuses on currently available technology for CO_2 capture at such plants. As before, the cost of CO_2 capture depends not only on the choice of capture technology, but more importantly on the characteristics and design of the overall power plant, including the fuel type and choice of gasifier. Because IGCC is not widely used for electric power generation at the present time , economic studies of IGCC power plants typically employ design assumptions based on the limited utility experience with IGCC systems, and the more extensive experience with gasification in industrial sectors such as petroleum refining and petrochemicals. For oxygen-blown gasifiers, the high operating pressure and relatively high CO_2 concentrations achievable in IGCC systems makes physical solvent absorption systems the predominant technology of interest for pre-combustion CO_2 capture (see Section 3.5.2.11). For purposes of cost reporting, we again distinguish between new plant designs and the retrofitting of existing facilities.

3.7.6.1 New Coal Gasification Combined Cycle Power Plants

Table 3.10 summarizes the key assumptions and results of several recent studies of CO_2 capture costs for new IGCC power plants ranging in size from approximately 400-800 MW net power output. While several gasifiers and coal types are represented, most studies focus on the oxygen-blown Texaco quench system,[10] and all but one assume bituminous coals. CO_2 capture efficiencies across these studies range from 85% to 92% using commercially available physical absorption systems. The energy requirements for capture increase the overall plant heat rate (energy input per kWh) by 16-25%, yielding net CO_2 reductions per kWh of 81-88%. Other study variables that influence total plant cost and the cost of CO_2 capture include the fuel cost, CO_2 product pressure, plant capacity factor and fixed charge factor. Many of the recent studies also include the cost of a spare gasifier to ensure high system reliability.

Table 3.10. CO_2 Capture Costs: New IGCC Power Plants with Current Capture Technology**.**

Table 3.10 indicates that for studies based on the Texaco or E-Gas gasifiers, CO_2 capture adds approximately 20-40% to both the capital cost (US$/kW) and the cost of electricity (US$/MWh) of the reference IGCC plants, while studies using the Shell gasifier report increases of roughly 30-65%. The total COE reported for IGCC systems ranges from 41-61 US$/MWh without capture and 54-79 US$/MWh with capture. With capture, the lowest COE is found for gasifier systems with quench cooling designs that have lower thermal efficiencies than the more capital-intensive designs with heat recovery systems. Without capture, however, the latter system type has the lowest COE in Table 3.10. Across all studies, the cost of CO_2 avoided ranges from 13-37 US$/tonne CO_2 relative to an IGCC without capture, excluding transport and storage costs. Part of the reason for this lower incremental cost of CO_2 capture relative to coal combustion plants is the lower average energy requirement for IGCC systems. Another key factor is the smaller gas volume treated in oxygen-blown gasifier systems, which substantially reduces equipment size and cost.

As with PC plants, Table 3.10 again underscores the importance of plant financing and utilization assumptions on the calculated cost of electricity, which in turn affects CO_2 capture costs. The lowest COE values in this table are for plants with a low fixed charge rate and high capacity factor, while substantially higher COE values result from high financing costs and lower plant utilization. Similarly, the type and properties of coal assumed has a major impact on the COE, as seen in a recent Canadian Clean Power Coalition study, which found substantially higher costs for low-rank coals using a Texaco-based IGCC system (Stobbs, 2005, Table 3.10). EPRI also reports higher IGCC costs for low-rank coals (Holt, et al, 2003). On the other hand, where plant-level assumptions

[10] In 2004, the Texaco gasifier was re-named as the GE gasifier following acquisition by GE Energy (General Electric). However, this report uses the name Texaco, as it is referred to in the original references cited.

and designs are similar across studies, there is relatively little difference in the estimated costs of CO_2 capture based on current commercial technology. Similarly, the several studies in Tables 3.7 and 3.10 that estimate costs for both IGCC and PC plants on an internally consistent basis all find that IGCC plants with capture have a lower COE than PC plants with capture. There is not yet a high degree of confidence in these cost estimates, however (see Table 3.6).

The costs in Table 3.10 also reflect efforts in some studies to identify least-cost CO_2 capture options. For example, one recent study (IEA GHG, 2003) found that capture and disposal of hydrogen sulfide (H_2S) along with CO_2 can reduce overall capture costs by about 20% (although this may increase transport and storage costs, as discussed in Chapters 4 and 5). The feasibility of this approach depends in a large part on applicable regulatory and permitting requirements. Advanced IGCC designs that may further reduce future CO_2 capture costs are discussed in Section 3.7.7.

3.7.6.2 Repowering of Existing Coal-Fired Plants with IGCC

For some existing coal-fired power plants, an alternative to the post-combustion capture systems discussed earlier is repowering with an IGCC system. In this case—depending on site-specific circumstances—some existing plant components, such as the steam turbine, might be refurbished and utilized as part of an IGCC plant. Alternatively, the entire combustion plant might be replaced with a new IGCC system while preserving other site facilities and infrastructure.

Although repowering has been widely studied as an option to improve plant performance and increase plant output, there are relatively few studies of repowering motivated by CO_2 capture. Table 3.8 shows results from one recent study (Chen, et.al, 2003) which reports CO_2 capture costs for IGCC repowering of a 250 MW coal-fired unit that is assumed to be a fully amortized (hence, a low COE of 21 US$/MWh). IGCC repowering yielded a net plant capacity of 600 MW with CO_2 capture, and a COE of 62-67 US$ depending on whether or not the existing steam turbine can be reused. The cost of CO_2 avoided was 46-51 US$/tonne CO_2. Compared to the option of retrofitting the existing PC unit with an amine-based capture system and retaining the existing boiler (Table 3.8), the COE for IGCC repowering was estimated to be 10% to 30% lower. These findings are in general agreement with earlier studies by Simbeck (1999). Because the addition of gas turbines roughly triples the gross plant capacity of a steam-electric plant, candidates for IGCC repowering are generally limited to smaller existing units (e.g., 100-300 MW). Taken together with the post-combustion retrofit studies in Table 3.8, the most cost-effective options for existing plants involve combining CO_2 capture with plant upgrades that increase overall efficiency and net output. Additional studies would be needed to systematically compare the feasibility and cost of IGCC repowering to supercritical boiler upgrades at existing coal-fired plants.

3.7.7 CO_2 capture cost for hydrogen production and multi-product plants (current technology)

While electric power systems have been the dominant technologies of interest for CO_2 capture studies, other industrial processes, including hydrogen production and multi-product plants producing a mix of fuels, chemicals and electricity also are of interest. Because CO_2 capture cost depends strongly on the production process in question, several categories of industrial processes are discussed below.

3.7.7.1 Hydrogen Production Plants

Section 3.5 discussed the potential role of hydrogen as an energy carrier, and the technological options for its production. Here we examine the cost of capturing CO_2 normally released during the production of hydrogen from fossil fuels. Table 3.11 shows the key assumptions and cost results of recent studies of CO_2 capture costs for plants with hydrogen production rates of 155,000 to 510,000

Nm^3/h (466-1531 MW_t), employing either natural gas or coal as a feedstock. The CO_2 capture efficiency for the hydrogen plant ranges from 87- 95% using commercially available chemical and physical absorption systems. The CO_2 reduction per unit of product is lower, however, because of the process energy requirements, and because of additional CO_2 emitted by an offsite power plant assumed in some of these studies. Because hydrogen production requires the separation of H_2 from CO_2, the incremental cost of capture is mainly the cost of CO_2 compression.

Table 3.11. CO_2 Capture Costs for Hydrogen and Multi-product Plants: Commercial or near-commercial technologies.

Today, hydrogen is produced mainly from natural gas. A recent study by the National Research Council (NRC, 2004) indicates that CO_2 capture would add approximately 18% to the unit cost of hydrogen while reducing net CO_2 emissions per unit of H_2 product by 83% (after accounting for the CO_2 emissions from imported electricity). The total cost of hydrogen is sensitive to the cost of feedstock, so different gas prices would alter both the absolute and relative costs of CO_2 capture. For coal-based hydrogen production, the NRC study projects an 8% increase in the unit cost of hydrogen for an 83% reduction in CO_2 emissions per unit of product. Again, this figure includes the CO_2 emissions from imported electricity.

3.7.7.2 Multi-Product Plants

Multi-product plants (also known as polygeneration plants) employ fossil fuel feedstocks to produce a variety of products such as electricity, hydrogen, chemicals and liquid fuels. To calculate the cost of any particular product (for a given rate of return), economic analyses of multi-product plants require that the selling price of all other products be specified over the operating life of the plant. Such assumptions, in addition to those discussed earlier, can significantly affect the outcome of cost calculations when there is not one dominant product at the facility.

Several of the coal-based hydrogen production plants in Table 3.11 also produce electricity, albeit in small amounts (in fact, smaller than the electricity quantities purchased by the stand-alone plants). Most of these studies assume that the value of the electricity product is higher under a carbon capture regime than without CO_2 capture. The result is a 5-21% increase in hydrogen production cost for CO_2 reductions of 83-96% per unit of product. The case with the lowest incremental product cost and highest CO_2 reduction assumes co-disposal of H_2S with CO_2, thus eliminating the costs of sulfur capture and recovery. As noted earlier (Section 3.7.6.1), the feasibility of this option depends strongly on local regulatory requirements; nor are higher costs for transport and storage reflected in the Table 3.11 cost estimate for this case.

Table 3.11 also presents examples of multi-product plants producing liquid fuels plus electricity. In these cases the amounts of electricity produced are sizeable compared to the liquid products, so the assumed selling price of electricity has a major influence on the product cost results. So too does the assumption in two of the cases of co-disposal of H_2S with CO_2 (as described above). For these reasons, the incremental cost of CO_2 capture ranges from a 13% decrease to a 13% increase in fuel product cost relative to the no-capture case. Note too that the overall level of CO_2 reductions per unit of product is only 27-56%. This is because a significant portion of carbon in the coal feedstock is exported with the liquid fuel products. Nonetheless, an important benefit of these fuel processing schemes is a reduction (of 30-38%) in the carbon content per unit of fuel energy relative to the feedstock fuel. To the extent these liquid fuels displace other fuels with higher carbon per unit of energy, there is a net benefit in end-use CO_2 emissions when the fuels are burned. However, no credit for such reductions is taken in Table 3.11 because the system boundary considered is confined to the fuel production plant.

3.7.8 Capture costs for other industrial processes (current technology)

CO_2 can be captured in other industrial processes using the techniques described earlier for power generation. While the costs of capture may vary considerably with the size, type and location of industrial processes, such costs will be lowest for processes or plants having: streams with relatively high CO_2 concentrations; process plants that normally operate at high load factors; plants with large CO_2 emission rates; and, processes that can utilize waste heat to satisfy the energy requirements of CO_2 capture systems. Despite these potential advantages, little detailed work has been carried out to estimate costs of CO_2 capture at industrial plants, with most work focused on oil refineries and petrochemical plants. A summary of currently available cost studies appears in Table 3.12.

Table 3.12. CO_2 Capture Costs: Other Industrial Processes with Current Capture Technology.

3.7.8.1 Oil Refining and Petrochemical Plants

Gas-fired process heaters and steam boilers are responsible for the bulk of the CO_2 emitted from typical oil refineries and petrochemical plants. Although refineries and petrochemical plants emit large quantities of CO_2, they include multiple emission sources often dispersed over a large area. Economies of scale can be achieved by using centralized CO_2 absorbers or amine regenerators but some of the benefits are offset by the cost of pipes and ducts. Based on Table 3.14, the cost of capturing and compressing CO_2 from refinery and petrochemical plant heaters using current technology is estimated to be 50-60 US$/tonne of CO_2 captured. Because of the complexity of these industrial facilities, along with proprietary concerns, the incremental cost of plant products is not normally reported.

High purity CO_2 is currently vented to the atmosphere by some gas processing and petrochemical plants, as described in Chapter 2. The cost of CO_2 capture in such cases would be simply the cost of drying and compressing the CO_2 to the pressure required for transport. The cost would depend on various factors, particularly the scale of operation and the electricity price. Based on 2 Mt/y of CO_2 and an electricity price of 5c/kWh, the cost is estimated to be around 10 US$/t of CO_2 emissions avoided. Electricity accounts for over half of the total cost.

3.7.8.2 Cement Plants

As noted in Chapter 2, cement plants are the largest industrial source of CO_2 apart from power plants. Cement plants normally burn lower cost high-carbon fuels such as coal, petroleum coke and various wastes. The flue gas typically has a CO_2 concentration of 14-33% by volume, significantly higher than at power plants, because CO_2 is produced in cement kilns by decomposition of carbonate minerals as well as by fuel combustion. The high CO_2 concentration would tend to reduce the specific cost of CO_2 capture from flue gas. Pre-combustion capture, if used, would only capture the fuel-related CO_2, so would be only a partial solution to CO_2 emissions. Oxyfuel combustion and capture using calcium sorbents are other options, which are described in sections 3.2.4 and 3.7.11.

3.7.8.3 Integrated Steel Mills

Integrated steel mills are some of the world's largest emitters of CO_2, as described in Chapter 2. About 70% of the carbon introduced into an integrated steel mill is contained in the blast furnace gas in the form of CO_2 and CO, each of which comprise about 20% by volume of the gas. The cost of capturing CO_2 from blast furnace gas was estimated to be 35 US$/tonne CO_2 avoided (Farla et. al., 1995) or 18 US$/tonne CO_2 captured (Gielen, 2003).

Iron ore can be reacted with synthesis gas or hydrogen to produce iron by direct reduction (Cheeley, 2000). Direct reduction processes are already used commercially but further development work would be needed to reduce their costs, to make them more widely competitive with conventional iron production processes. The cost of capturing CO_2 from a direct reduction reduction iron (DRI) production processes was estimated to be 10 US$/t CO_2 (Gielen, 2003). CO_2 also could be captured from other gases in iron and steel mills but costs would probably be higher as they are more dilute or smaller in scale.

3.7.8.4 Biomass plants

The main large point sources of biomass-derived CO_2 are currently wood pulp mills, which emit CO_2 from black liquor recovery boilers and bark-fired boilers, and sugar/ethanol mills, which emit CO_2 from bagasse-fired boilers. Black liquor is a by-product of pulping that contains lignin and chemicals used in the pulping process. The cost of post combustion capture was estimated to be 34 US$/tonne of CO_2 avoided in a plant that captures about 1 Mt/y of CO_2 (Möllersten et.al., 2003). Biomass gasification is under development as an alternative to boilers.

CO_2 could be captured from sucrose fermentation and from combustion of sugar cane bagasse at a cost of about 53 US$/tonne CO_2 avoided for a plant capturing 0.6 Mt CO_2/y avoided (Möllersten et.al., 2003). CO_2 from sugar cane fermentation has a high purity, so only drying and compression is required. The overall cost is relatively high due to an annual load factor that is lower than that of most power stations and large industrial plants.

CO_2 could be captured at steam-generating plants or power plants that use other biomass by-products and/or purpose-grown biomass. At present most biomass plants are relatively small. The cost of capturing 0.19 Mt/y of CO_2 in a 24 MW biomass-powered IGCC plant, compared to a biomass IGCC plant without capture, is estimated to be about 70 US$/tonne of CO_2 (Audus and Freund, 2005). Larger plants using purpose-grown biomass may be built in the future, and biomass can be co-fired with fossil fuels to give economies of scale, as discussed in Chapter 2. Biomass fuels produce similar or slightly greater quantities of CO_2 per unit of fuel energy as bituminous coals; thus, the CO_2 concentration of flue gases from these fuels will be broadly similar. This implies that the cost of capturing CO_2 at large power plants using biomass may be broadly similar to the cost of capturing CO_2 in large fossil fuel power plants in cases where plant size, efficiency, load factor and other key parameters are similar. The costs of avoiding CO_2 emissions in power plants that use biomass are discussed in more detail in Chapter 8.

CO_2 also could be captured in biomass-fuelled hydrogen production plants. The cost is reported to be 11 US$/tonne of CO_2 captured in a plant producing 1 million Nm^3/d of hydrogen (Makihira, 2003).

3.7.9 Outlook for future CO_2 capture costs

The following sections focus on “advanced” technologies that are not yet commercial available, but which promise to lower CO_2 capture costs based on preliminary data and design studies. Earlier sections of Chapter 3 discussed some of the efforts underway worldwide to develop lower-cost options for CO_2 capture. Some of these developments are based on new process concepts, while others represent improvements to current commercial processes. Indeed, the history of technology innovation indicates that incremental technological change, sustained over many years (often decades), is often the most successful path to substantial long-term improvements in performance and reductions in cost of a technology (Alic, et al, 2003). Such trends are commonly represented and quantified in the form of a “learning curve” or “experience curve” showing cost reductions as a function of the cumulative adoption of a particular technology (McDonald and Schrattenholzer,

2001). One recent study relevant to CO_2 capture systems found that over the past 25 years capital costs for sulfur dioxide (SO_2) and nitrogen oxides (NO_x) capture systems at U.S. coal-fired power plants decreased an average of 12% for each doubling of installed worldwide capacity (a surrogate for cumulative experience, including investments in R&D) (Rubin, et.al, 2004a). These capture technologies bear a number of similarities to current systems for CO_2 capture. Another recent study (IEA, 2004) suggests a 20% cost reduction for a doubling of the unit capacity of engineered processes due to technological learning. For CCS systems the importance of costs related to energy requirements is emphasized since reductions in such costs are required to significantly reduce the overall cost of CO_2 capture.

At the same time, a large body of literature on technology innovation also teaches us that learning rates are highly uncertain,[11] and that cost estimates for technologies at the early stages of development are often unreliable and overly optimistic (Merrow, et. al, 1981). Qualitative descriptions of cost trends for advanced technologies and energy systems typically show costs increasing from the research stage through full-scale demonstration; only after one or more full-scale commercial plants are deployed do costs begin to decline for subsequent units (EPRI, 1993; NRC, 2003). Case studies of the SO_2 and NO_x capture systems noted above showed similar behavior, with large (factor of two or more) increases in the cost of early full-scale FGD and SCR installations before costs subsequently declined (Rubin, et.al, 2004b). Thus, cost estimates for CO_2 capture systems should be viewed in the context of their current stage of development. We attempt here to provide a perspective on potential future costs that combines qualitative judgments with the quantitative cost estimates offered by technology developers and analysts. The sections below re-visit the areas of power generation and other industrial processes to highlight some of the major prospects for CO_2 capture cost reductions.

3.7.10 CO_2 capture costs for electric power plants (advanced technology)

This section first examines oxy-fuel combustion, which avoids the need for CO_2 capture by producing a concentrated CO_2 stream for delivery to a transport and storage system. Following this we examine potential advances in post-combustion and pre-combustion capture.

3.7.10.1 Oxy-fuel Combustion Systems

It is first important to distinguish between two types of oxy-fuel systems: an oxy-fuel boiler (either a retrofit or new design) and oxy-fuel combustion-based gas turbine cycles. The former are close to demonstration at a commercial scale, while the latter (such as chemical looping combustion systems and novel power cycles using CO_2/water as working fluid) are still at the design stage. Table 3.13 summarizes the key assumptions and cost results of several recent studies of CO_2 capture costs for oxy-fuel combustion systems applied to new or existing coal-fired units. As discussed earlier in Section 3.4, oxygen combustion produces a flue gas stream consisting primarily of CO_2 and water vapor, along with smaller amounts of SO_2, nitrogen and other trace impurities. These designs eliminate the capital and operating costs of a post-combustion CO_2 capture system, but new costs are incurred for the oxygen plant and other system design modifications. Because oxy-fuel combustion is still under development and has not yet been utilized or demonstrated for large-scale power generation, the design basis and cost estimates for such systems remain highly variable and uncertain. This is reflected in the wide range of oxy-fuel cost estimates in Table 3.13. Note, however, that cost estimates for advanced design concepts based on oxy-fuel combustion gas

[11] In their study of 42 energy-related technologies, McDonald and Schrattenholzer (2001) found learning rates varying from -14% to 34%, with a median value of 16%. These rates represent the average reduction in cost for each doubling of installed capacity. A negative learning rate indicates that costs increased rather than decreased over the period studied.

turbine cycles are more uncertain at this time than cost estimates for new or retrofitted boilers employing oxy-fuel combustion.

Table 3.13. CO_2 Capture Costs: Advanced Technologies for Electric Power Plants.

For new plant applications, the data in Table 3.13 indicate that oxy-fuel combustion adds about 30-90% to the capital cost and 30-150% to the COE of a conventional plant, while reducing CO_2 emissions per kWh by 75-100%. Retrofit applications exhibit higher relative costs in cases where the existing plant is wholly or partially amortized. The lowest-cost oxy-fuel system in Table 3.13 is one that employs chemical looping to achieve nearly a 100% reduction in CO_2 emissions. While this concept thus appears promising (see Section 3.4.6), it has yet to be tested and verified at a meaningful scale. Thus, cost estimates based on conceptual designs remain highly uncertain at this time.

To judge the potential cost savings of oxy-fuels relative to current CO_2 capture systems, it is useful to compare the costs of alternative technologies evaluated within a particular study based on a particular set of premises. In this regard, the COE for the oxy-fuel retrofit system reported by Alstom et.al (2001) in Table 3.13 is 20% lower than the cost of an amine system retrofit (Table 3.13) for the same 255 MW plant, while the cost of CO_2 avoided is 26% lower. In contrast, a recent study by the Canadian Clean Power Coalition (Stobbs, 2005) reports that the COE for an oxy-fuel system at a large lignite-fired plant (Table 3.13) is 36% higher than for an amine CO_2 capture system, while the cost of CO_2 avoided is more than twice as great. The major source of that cost difference was a specification in the CCPC study that the oxy-fueled unit also be capable of full air firing. This resulted in a much higher capital cost than for a new unit designed only for oxy-fuel operation. A more recent study sponsored by IEA GHG (Dillon, et.al, 2005) found that a large new supercritical coal-fired boiler with oxy-fuel combustion had a COE slightly (2-3%) lower than a state-of-the-art coal plant with post-combustion analyzed in a separate study employing similar assumptions (IEA GHG, 2004). Further cost reductions could be achieved with the successful development of new lower-cost oxygen production technology (see Section 3.4.5). At the current time, the optimum designs of oxy-fuel combustion systems are not yet well established, and costs of proposed commercial designs remain uncertain. This is especially true for advanced design concepts that employ components that are not yet available or still in the development stage, such as CO_2 gas turbines or high temperature ceramic membranes for oxygen production.

3.7.10.2 Advanced Systems with Post-Combustion Capture

Improvements to current amine-based systems for post-combustion CO_2 capture are being pursued by a number of process developers (Mimura et. al., 2003; Muramatsu and Iijima, 2003; Reddy et.al, 2003), and may offer the nearest-term potential for cost reductions over the systems currently in use. The newest systems summarized earlier in Table 3.7 reportedly reduce the cost of CO_2 avoided by approximately 20-30% (IEA GHG, 2004). Table 3.13 indicates that additional advances in plant heat integration could further reduce the COE of capture plants by about 5%. These results are consistent with a recent study by Rao, et.al (2003), who used expert elicitations and a plant simulation model to quantify the improvements likely achievable by 2015 for four key process parameters: sorbent concentration, regeneration energy requirements, sorbent loss, and sorbent cost. The "most likely" improvement was an 18% reduction in COE, while the "optimistic" estimates yielded a 36% cost reduction from improvements in just these four parameters. The cost of CO_2 avoided was reduced by similar amounts. Advances in more efficient heat integration (for sorbent regeneration) and higher power plant efficiency could lead to even greater reductions in CO_2 capture cost.

Advances in gas turbine technology produce similar benefits for NGCC systems. Table 3.13 shows several cases based on the H-turbine design. Relative to the cases in Table 3.9, these systems offer higher efficiency and greater CO_2 reductions per kWh. The higher COEs for the advanced NGCC systems reflects the higher natural gas prices assumed in more recent studies.

Table 3.13 indicates that other advanced technologies for post-combustion applications, such as membrane separation systems, also may lower the future cost of CO_2 capture (see Section 3.3.3). Reliable cost estimates for such technologies should await their further development and demonstration.

3.7.10.3 Advanced Systems with Pre-Combustion Capture

The cost of gasification-based systems with CO_2 capture also can be expected to fall as a result of continued improvements in gas turbine technology, gasifier designs, oxygen production systems, carbon capture technology, energy management, and optimization of the overall facility. One recent study (IEA GHG, 2003) estimates a 20% reduction in the cost of electricity generation from a coal-based IGCC plant with CO_2 capture by 2020. This takes into account improvements in gasification, oxygen production, physical solvent scrubbing and combined cycle processes, but does not take into account any possible radical innovations in CO_2 separation technology. The additional IGCC cases shown in Table 3.13, including recent results of the CO_2 Capture Project (CCP, 2005), foresee similar reductions in the COE of advanced IGCC systems compared to the systems in Table 3.10.

3.7.11 CO_2 capture costs for hydrogen production and multi-product plants (advanced technology)

Table 3.14 shows results of several recent studies that have projected the performance and cost of new or improved ways of producing hydrogen and electricity from fossil fuels.

Table 3.14. CO_2 Capture Costs for Multi-product Plants: Advanced Technologies.

Compared to the current commercial plants in Table 3.11, the advanced single-product systems with CO_2 capture have hydrogen cost reductions of 16% (for natural gas feedstock) to 26% (for coal feedstock). Additional cases in Table 3.14 show multi-product systems producing hydrogen and electricity. These cases indicate the potential for substantial reductions in the future cost of hydrogen production with CO_2 capture. As before, the results are sensitive to the assumed selling price of co-product electricity. More importantly, these cases assume the successful scale-up and commercialization of technologies that have not yet been demonstrated, or which are still under development at relatively small scales, such as solid oxide fuel cells (SOFC). Published cost estimates for these systems thus have a very high degree of uncertainty.

3.7.12 CO_2 capture costs for other industrial processes (advanced technology)

As noted earlier, CO_2 capture for industrial processes has not been widely studied. The most extensive analyses have focused on petroleum refineries, especially CO_2 capture options for heaters and other combustion-based processes (see Table 3.12). The use of oxyfuel combustion offers potential cost savings in several industrial applications. The CO_2 Capture Project reports the cost of capturing CO_2 in refinery heaters and boilers, with an ion transport membrane oxygen plant, to be 31 US$/tonne CO_2 avoided. The cost of pre-combustion capture based on shift and membrane gas separation was predicted to be 41 US$/tonne CO_2 avoided (CCP, 2005).

It also may be possible to apply oxy-fuel combustion to cement plants, but the CO_2 partial pressure in the cement kiln would be higher than normal and the effects of this on the calcination reactions

and the quality of the cement product would need to be investigated. The quantity of oxygen required per tonne of CO_2 captured in a cement plant would be only about half as much as in a power plant, because only about half of the CO_2 is produced by fuel combustion. This implies that the cost of CO_2 capture by oxy-fuel combustion at large cement plants would be lower than at power plants, but a detailed engineering cost study is lacking. Emerging technologies that capture CO_2 using calcium-based sorbents, described in Section 3.3.3.4, may be cost competitive in cement plants in the future.

3.7.13 Summary of CO_2 capture cost estimates

Table 3.15 summarizes the range of current CO_2 capture costs for the major electric power systems analyzed in this report. These costs apply to case studies of large new plants employing current commercial technologies. For the PC and IGCC systems, the data in Table 3.15 apply only to plants using bituminous coals, and the PC plants are for supercritical units only. The cost ranges for each of the three systems reflect differences in the technical, economic and operating assumptions employed in different studies. While some differences in reported costs can be attributed to differences in the CO_2 capture system design, the major sources of variability are differences in the assumed design, operation and financing of the reference plant to which the capture technology is applied (i.e., factors such as plant size, location, efficiency, fuel type, fuel cost, capacity factor and cost of capital). Because no single set of assumptions applies to all situations or all parts of the world, we display the ranges of cost represented by the studies in Tables 3.8, 3.10, 3.11 and 3.12.

Table 3.15. Summary of CO_2 Capture Costs for New Plants Based on Current Technology.

For the power plant studies reflected in Table 3.15, current CO_2 capture systems reduce CO_2 emissions per kilowatt-hour by approximately 85-90% relative to a similar plant without capture. The cost of electricity production attributed to CO_2 capture increases by 35-70% for a natural gas combined cycle plant, 40-85% for a new pulverized coal plant, and 20-55% for an integrated gasification combined cycle plant. Overall, the COE for fossil fuel plants with capture ranges from 43-86 US$/MWh, as compared to 31-61 US$/MWh for similar plants without capture. These costs include CO_2 compression but not transport and storage costs. In most studies to date, NGCC systems typically have a lower COE than new PC and IGCC plants (with or without capture) for large base load plants with high capacity factors (75% or more) and gas prices below about 4 US$/GJ over the life of the plant. However, for higher gas prices and/or lower capacity factors, NGCC plants typically have higher COEs than coal-based plants, with or without capture. Recent studies also found that IGCC plants were on average slightly more costly without capture and slightly less costly with capture than similarly sized PC plants. However, the difference in cost between PC and IGCC plants with or without CO_2 capture can vary significantly with coal type and other local factors, such as the cost of capital. Since neither PC nor IGCC systems have yet been demonstrated with CO_2 capture and storage for a large modern power plant (e.g., 500 MW), neither the absolute or relative costs of these systems (nor comparably sized NGCC systems with capture and storage) can be stated with a high degree of confidence at this time, based on the criteria of Table 3.6.

Table 3.15 also shows that the lowest CO_2 capture costs with current technology (as low as 2 US$/tonne of CO_2 captured or avoided) were found for industrial processes such as coal-based hydrogen production plants that produce concentrated CO_2 streams as part of the production process. Such industrial processes may represent some of the earliest opportunities for CCS.

Figure 3.20 displays the normalized power plant cost and emissions data from Table 3.15 in graphical form. On this graph, the cost of CO_2 avoided corresponds to the slope of a line connecting

any two plants (or points) of interest. While Table 3.15 compares a given capture plant to a similar plant without capture, in some cases comparisons may be sought between a given capture plant and a different type of reference plant. Several cases are illustrated in Figure 3.20 based on either a PC or NGCC reference plant. In each case, the COE and CO_2 emission rate are highly dependent upon technical, economic and financial factors related to the design and operation of the power systems of interest at a particular location. The cost of CO_2 avoided is especially sensitive to these site-specific factors, and can vary by an order of magnitude or more when different types of plants are compared. Comparisons of different plant types, therefore, require a specific context and geographical location to be meaningful, and should be based on the full COE including CO_2 transport and storage costs. Later, Chapter 8 presents examples of full CCS costs for different plant types and storage options.

Figure 3.20. Cost of electricity (excluding transport and storage costs) vs. CO_2 emission rate for different reference and capture plants based on current technology. The shaded areas show the Table 3.15 ranges of CO_2 emission rates and levelized cost of electricity (COE) for new PC, IGCC and NGCC plants with and without CO_2 capture. All coal plant data are for bituminous coals only. PC plants are supercritical units only. (See Tables 3.7, 3.9, 3.10 and 3.15 for additional assumptions.) The cost of CO_2 avoided corresponds to the slope of a line connecting a plant with capture and a reference plant without capture (i.e., the change in electricity cost divided by the change in emission rate). Avoidance costs for the same type of plant with and without capture plant are given in Table 3.15. When comparing different plant types, the reference plant represents the least-cost plant that would "normally" be built at a particular location in the absence of a carbon constraint. In many regions today, this would be either a PC plant or an NGCC plant. The cost per tonne of CO_2 avoided can be highly variable, and depends strongly on the costs and emissions of new plants being considered in a particular situation. See Chapter 8 for the full COE and full cost of CO_2 avoided for different plant types.

In contrast to new plants, CO_2 capture options and costs for existing power plants have not been extensively studied. Current studies indicate that these costs are extremely site-specific, and fall into two categories (see Table 3.8). One is the retrofitting of a post-combustion capture system to the existing unit. The other category combines CO_2 capture with upgrading or repowering the existing plant to significantly improve its efficiency and net power output (see Sections 3.7.4.2 and 3.7.5.2). In general, the latter option appears to be more cost-effective. However, further site-specific studies are required to systematically assess the feasibility and cost of alternative repowering options in conjunction with CO_2 capture for existing power plants.

New or improved methods of CO_2 capture, combined with advanced power systems and industrial process designs, promise to significantly reduce CO_2 capture costs and associated energy requirements. Tables 3.12 to 3.14 summarize the results from recent studies that examine future options. As discussed earlier, there is considerable uncertainty about the magnitude and timing of future cost reductions, as well as the potential for costs to rise above current estimates, especially for technologies still in the early stages of research and development. The current assessment is based on studies of the specific technologies in Tables 3.12 to 3.14 (and the supporting discussions and literature cited in Sections 3.7.9 to 3.7.12), as well as analyses of historical cost trends for related energy and environmental technologies. This assessment suggests that improvements to current commercial technologies can reduce CO_2 capture costs by at least 20-30% over approximately the next decade, while new technologies under development promise more substantial cost reductions. Achieving future cost reductions, however, will require deployment and adoption of commercial technologies in the marketplace as well as sustained R&D

3.8 Gaps in knowledge

Gaps in knowledge are related to differences in the stages of development of component technologies for the capture systems reviewed in Sections 3.2 - 3.5. For CO_2 capture from industrial processes, a number of technologies that are commonly used in gas sweetening and ammonia production are already used on a commercial scale. For other types of industrial systems capturing CO_2 from steel and cement production further work is still needed. For CO_2 capture that might be reliant on post combustion capture or oxy-fuel combustion, options are less well developed, or are available at a smaller scale than those required for applications such as in power generation, where much larger gas flows are handled. For pre-combustion capture many of the required systems have been developed and applied in industry already.

Although many of the component and/or enabling technologies required for CO_2 capture in post combustion, pre-combustion and oxy-fuel combustion are well known, gaps in knowledge are in the practical and/or commercial demonstration of integrated systems. This demonstration is essential to prove the cost of CO_2 capture and its use on a large scale, particularly in power generation applications, but also for cement, steel and other large industries. Operating experience is also needed to test system reliability, improved methods of system integration, methods to reduce the energy requirements for CO_2 capture, improved process control strategies, and the use of optimised functional materials for the implementation of capture processes with advanced, higher efficiency power cycles. As such developments are realized, environmental issues associated with the capture of CO_2 and other deleterious pollutants in these systems should also be re-assessed from a perspective involving the whole capture-transport-storage operation.

In an ongoing search to implement existing, new or improved methods of CO_2 capture, most capture systems also rely on the application of a range of enabling technologies that influence the attractiveness of a given system. These enabling technologies have their own critical gaps of knowledge. For example improved processes for the effective removal of sulphur, nitrogen, chlorine, mercury and other pollutants are needed for the effective performance of unit operations for CO_2 separation in post and pre-combustion capture systems, especially when using coal as the primary fuel. Improved gasification reactors for coals and biomass, the availability of hydrogen-burning gas turbines and fuel cells for stationary power generation also need further development in the pre-combustion route. Combustors and boilers operating at higher temperatures, or a new class of CO_2 turbines and compressors, are important requirements for oxy-fuel systems.

With reference to the development of novel CO_2 capture and/or other enabling technologies, a wide range of options are currently being investigated worldwide. However, many technical details of the specific processes proposed or under development for these emerging technologies are still not well understood. This makes the assessment of their performance and cost highly uncertain. Here is where intense R&D is needed to develop and bring to pilot scale testing the most promising concepts for commercial application. Membranes for H_2, CO_2 or O_2 separation, new sorbents, O_2 or CO_2 solid carriers, and materials for advanced combustors, boilers and turbines all require extensive performance testing. Multi-pollutant emission controls in these novel systems, and the impact of fuel impurities and temperature on the functional materials, should also be an area of future work.

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Tables

Table 3.1. Capture toolbox.

	Process streams[a]		**Post-combustion capture**		**Oxy-fuel combustion capture**		**Pre-combustion capture**	
Separation task	CO_2/CH_4		CO_2/N_2		O_2/N_2		CO_2/H_2	
Capture Technologies	Current	Emerging	Current	Emerging	Current	Emerging	Current	Emerging
Solvents (Absorption)	**Physical solvents** **Chemical solvents**	Improved solvents Novel contacting equipment Improved design of processes	**Chemical solvents**	Improved solvents Novel contacting equipment Improved design of processes	n. a.	Biomimetic solvents, e.g. hemoglobine-derivatives	**Physical solvent** **Chemical solvents**	Improved chemical solvents Novel contacting equipment Improved design of processes
Membranes	**Polymeric**	Ceramic Facilitated transport Carbon Contactors	Polymeric	Ceramic Facilitated transport Carbon Contactors	Polymeric	Ion transport membranes Facilitated transport	Polymeric	Ceramic Palladium Reactors Contactors
Solid sorbents	Zeolites Activated carbon		Zeolites Activated carbon	Carbonates Carbon based sorbents	Zeolites Activated carbon	Adsorbents for O_2/N_2 separation, Perovskites **Oxygen chemical looping**	Zeolites Activated carbon Alumina	Carbonates Hydrotalcites Silicates
Cryogenic	Ryan-Holmes process		Liquefaction	Hybrid processes	**Distillation**	Improved distillation	Liquefaction	Hybrid processes

[a] Notes: Processes shown in bold are commercial processes that are currently preferred in most circumstances. Some process streams involve CO_2/H_2 or CO_2/N_2 separations but this is covered under pre-combustion capture and post combustion capture. The key separation processes are outlined in Section 3.1.3 and described in Sections 3.2-3.5.

Table 3.2. Common solvents used for the removal of CO_2 from shifted syngas in pre-combustion capture processes.

Solvent name	Type	Chemical name	Vendors
Rectisol	Physical	Methanol	Lurgi and Linde, Germany Lotepro Corporation, USA
Purisol	Physical	N - methyl - 2 - pyrolidone (NMP)	Lurgi, Germany
Selexol	Physical	Dimethyl ethers of polyethylene glycol (DMPEG)	Union Carbide, USA
Benfield	Chemical	Potassium carbonate	UOP
MEA	Chemical	Monoethanolamine	Various
MDEA	Chemical	Methyldiethylamine	BASF and others
Sulfinol	Chemical	Tetrahydrothiophene 1,1-dioxide (Sulfolane), an alkaloamine and water	Shell

Table 3.3. Membrane materials, operating conditions and characteristics for H_2 separation.

	Micro porous Ceramic	Micro porous Ceramic	Micro porous Carbon	Zeolites	Metal
Membrane material	Alumina	Silica	Carbon	Silica (Alumina)	Pd/Ag
Temperature range (°C)	< 500	< 400	< 400	< 500 – 700	< 600
Pressure range (bar)	> 100	> 100	10	> 100	> 100
Pore size distribution (nm)	0.7 - 2	0.7 - 2	0.7 - 2	0.3 - 0.7	no pores
Separation factors (H_2/CO_2)	15	15	15 - 25	50	100
Permeability (mol/m^2sPa)	10^{-6}	10^{-6}	10^{-7}	10^{-6}	10^{-7} - 10^{-6}
Experim. temp. (°C)	200	200	300 - 400	300 - 400	300 - 400
Pre-cleanup requirements				S	S, HCl, HF (?)
Chemical resistance problem		H_2O	O_2	S	S, HCl, HF
Geometry	Top layer tube	Top layer tube	Top layer tube/fibre	Top layer tube	Top layer tube/plate
Configuration	Cascade /recycle/once through	Cascade /recycle/once through	Cascade /recycle/once through	Once through	Once through
Life time	+	-	+	+	0
Costs ($\$/m^2$)	4250	4250	3000?	4000 – 4250	4000 - 4250
Scalability	0	0	0	-	0

Table 3.4. Concentrations of impurities in dried CO_2, vol. % (Source data: IEA GHG 2003, IEA GHG 2004, IEA GHG 2005).

	SO_2	NO	H_2S	H_2	CO	CH_4	$N_2/Ar/O_2$	Total
COAL FIRED PLANTS								
Post-combustion capture	<0.01	<0.01	0	0	0	0	0.01	0.01
Pre-combustion capture (IGCC)	0	0	0.01-0.6	0.8-2.0	0.03-0.4	0.01	0.03-0.6	2.1-2.7
Oxy-fuel	0.5	0.01	0	0	0	0	3.7	4.2
GAS FIRED PLANTS								
Post-combustion capture	<0.01	<0.01	0	0	0	0	0.01	0.01
Pre-combustion capture	0	0	<0.01	1.0	0.04	2.0	1.3	4.4
Oxy-fuel	<0.01	<0.01	0	0	0	0	4.1	4.1

a. The SO_2 concentration for oxy-fuel and the maximum H_2S concentration for pre-combustion capture are for cases where these impurities are deliberately left in the CO_2, to reduce the costs of capture (see Section 3.6.1.1). The concentrations shown in the table are based on use of coal with a sulphur content of 0.86%. The concentrations would be directly proportional to the fuel sulphur content.

b. The oxy-fuel case includes cryogenic purification of the CO_2 to separate some of the N_2, Ar, O_2 and NO_x. Removal of this unit would increase impurity concentrations but reduce costs.

c. For all technologies, the impurity concentrations shown in the table could be reduced at higher capture costs.

Table 3.5. Illustrative impacts of CCS energy requirements on plant-level resource consumption and non-CO_2 emission rates for three current power plant systems. Values shown are mass flow rates per MWh for the capture plant, plus increases over the reference plant rates for the same plant type. See footnotes for additional details. (Source: Rubin *et al.*, 2005)

Capture Plant Parameter [a]	PC [b]		IGCC [c]		NGCC [d]	
	Rate	Increase	Rate	Increase	Rate	Increase
Resource Consumption (all values in kg/MWh)						
Fuel	390	93	361	49	156	23
Limestone	27.5	6.8	-	-	-	-
Ammonia	0.80	0.19	-	-	-	-
CCS Reagents	2.76	2.76	0.005	0.005	0.80	0.80
Solid Wastes/ Byproduct						
Ash/slag	28.1	6.7	34.2	4.7	-	-
FGD residues	49.6	12.2	-	-	-	-
Sulfur	-	-	7.53	1.04	-	-
Spent CCS sorbent	4.05	4.05	0.005	0.005	0.94	0.94
Atmospheric Emissions						
CO_2	107	*–704*	97	*–720*	43	*–342*
SO_x	0.001	*– 0.29*	0.33	0.05	-	-
NO_x	0.77	0.18	0.10	0.01	0.11	0.02
NH_3	0.23	0.22	-	-	0.002	0.002

[a] Net power output of all plants is approximately 500 MW. Coal plants use Pittsburgh #8 coal with 2.1%S, 7.2% ash, 5.1% moisture and 303.2 MJ/kg lower heating value basis (LHV). Natural gas LHV = 59.9 MJ/kg. All plants capture 90% of potential CO_2 emissions and compress to 13.7 MPa.

[b] PC= Pulverized coal-fired plant; based on a supercritical unit with SCR, ESP and FGD systems, followed by an amine system for CO_2 capture. SCR system assumes 2 ppmv ammonia slip. SO_2 removal efficiency is 98% for reference plant and 99% for capture plant. Net plant efficiency (LHV basis) is 40.9% without CCS and 31.2% with CCS.

[c] IGCC=integrated gasification combined cycle system based on Texaco quench gasifiers (2 + 1 spare), two GE 7FA gas turbines, 3-pressure reheat HRSG. Sulfur removal efficiency is 98% via hydrolyzer plus Selexol system; Sulfur recovery via Claus plant and Beavon-Stretford tailgas unit. Net plant efficiency (LHV basis) is 39.1% without CCS and 33.8% with CCS.

[d] NGCC=natural gas combined cycle plant using two GE 7FA gas turbines and 3-pressure reheat HRSG, with an amine system for CO_2 capture. Net plant efficiency (LHV basis) is 55.8% without CCS and 47.6% with CCS.

Table 3.6. Confidence levels for technology and system cost estimates.

Confidence Level	Description
Very High	Mature technology with multiple commercial replications for this application and scale of operation; considerable operating experience and data under a variety of conditions.
High	Commercially deployed in applications similar to the system under study, but at a smaller scale and/or with limited operating experience; no major problems or issues anticipated in this application; commercial guarantees available.
Moderate	No commercial application for the system and/or scale of interest, but technology is commercially deployed in other applications; issues of scale-up, operability and reliability remain to be demonstrated for this application.
Low	Experience and data based on pilot plant or proof-of-concept scale; no commercial applications or full-scale demonstrations; significant technical issues or cost-related questions still to be resolved for this application.
Very Low	A new concept or process not yet tested, or with operational data limited to the laboratory or bench-scale level; issues of large-scale operability, effectiveness, reliability and manufacturability remain to be demonstrated.

Table 3.7. CO_2 Capture Costs: New Pulverized Coal Power Plants using Current Technology.

Study Assumptions and Results	Parsons	Parsons	Simbeck	IEA GHG	IEA GHG	Rubin et al	Range		NETL	Rao & Rubin	Stobbs
	2002b	2002b	2002	2004	2004	2005	min	max	2002	2002	2005
	SUPERCRITICAL UNITS w/ BITUMINOUS COALS								SUBCRIT UNITS / LOW RANK COALS		
Reference Plant (w/o capture)			*			*			*	*	
Boiler type (subcritical, super, ultra)	super	ultra	ultra	ultra	ultra	super			subcritcal	subcritcal	super
Coal type (bit, subbit, lig) and %S	bit, 2.5% S	bit, 2.5% S	bit, 1% S	bit, 1% S	bit, 1% S	bit, 2.1% S			bit, 2.5%S	subbit, 0.5%S	lignite
Emission control technologies (SO_2/NO_x)	FGD, SCR	FGD, SCR	FGD, SCR	FGD, SCR	FGD, SCR	FGD, SCR			FGD	FGD, SCR	FGD, SCR, LoTOx
Reference plant net output (MW)	462	506	520	758	754	524	**462**	**758**	397	462	424
Plant capacity factor (%)	65	65	80	85	85	75	**65**	**85**	85	75	90
Net plant efficiency, LHV (%)	42.2	44.8	44.5	44.0	43.7	40.9	**41**	**45**	38.9	36.1	43.4
Coal cost, LHV (US$/GJ)	1.29		*0.98*	1.50	1.50	1.25	**0.98**	**1.50**	*1.03*	*1.25*	0.88
Reference plant emission rate (t CO_2/MWh)	0.774	0.736	0.76	0.743	0.747	0.811	**0.74**	**0.81**	0.835	0.941	0.883
Capture Plant Design											
CO_2 capture technology	MEA	MEA	MEA	MEA	KS-1	MEA			MEA	MEA	MEA
Net plant output with capture (MW)	329	367	408	666	676	492	**329**	**676**	283	326	311.0
Net plant efficiency, LHV (%)	30.1	32.5	*34.9*	34.8	35.4	31.1	**30**	**35**	27.7	*25.4*	31.8
CO_2 capture system efficiency (%)	90	90	85	87.5	90	90	**85**	**90**	95	90	95
CO_2 emission rate after capture (t/MWh)	0.108	0.101	0.145	0.117	0.092	0.107	**0.09**	**0.15**	0.059	0.133	0.060
CO_2 captured (Mt/yr)	1.830	2.350	2.360	4.061	4.168	3.102	**1.83**	**4.17**	2.346	2.580	2.795
CO_2 product pressure (MPa)	8.4	8.4	13.7	11.0	11.0	13.9	**8**	**14**	10.3	13.9	13.9
CCS energy reqm't. (% more input/MWh)	40	38	28	26	24	31	**24**	**40**	40	42	36
CO_2 reduction per kWh (%)	**86**	**86**	**81**	**84**	**88**	**87**	**81**	**88**	**93**	**86**	**93**
Cost Results			***	**	**						***
Cost year basis (constant dollars)	2000	2000	2000	2004	2004	2002			2002	2000	2003
Fixed charge factor (%)	15.5	15.5	*12.7*	11.0	11.0	14.8	**11.0**	**15.5**	14.8	15.0	
Reference plant TCR (US$/kW)	1281	1161	*1486*	*1319*	*1265*	1205	**1161**	**1486**	1268	1236	*1891*
Capture plant TCR (US$/kW)	2219	1943	*2578*	*1894*	*2007*	1936	**1894**	**2578**	2373	2163	*3252*
Incremental TCR for capture (US$/kW)	938	782	*1092*	*575*	*742*	731	**575**	**1092**	1105	927	*1361*
Reference plant COE (US$/MWh)	**51.5**	**51.0**	**42.9**	**43.9**	**42.8**	**46.1**	**43**	**52**	**42.3**	**49.2**	**44.5**
Capture plant COE (US$/MWh)	**85.6**	**82.4**	**70.9**	**62.4**	**63.0**	**74.1**	**62**	**86**	**76.6**	**87.0**	**74.3**
Incremental COE for capture (US$/MWh)	**34.1**	**31.4**	**28**	**18.5**	**20.2**	**28**	**18**	**34**	**37.8**	**37.8**	**29.8**
% increase in capital cost (over ref. plant)	73	67	74	44	59	61	**44**	**74**	87	75	72
% increase in COE (over ref. plant)	**66**	**62**	**65**	**42**	**47**	**61**	**42**	**66**	**81**	**77**	**67**
Cost of CO_2 captured (US$/t CO_2)	35	28	34	23	24	29	**23**	**35**	31	31	26
Cost of CO_2 avoided (US$/t CO_2)	51	49	43	29	31	40	**29**	**51**	43	47	36
Capture Cost Confidence Level (see Table 3.6)	- moderate -								- moderate -		

Notes: All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. Values in italics were adjusted from original reported values as explained below. * *Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal. ** Reported capital costs increased by 8% to include interest during construction. ***Reported capital costs increased by 15% to estimate interest during construction and other owners' costs.*

Table 3.8. CO_2 Capture Costs: Existing Pulverized Coal Power Plants using Current Technology.

Study Assumptions and Results	Simbeck	Alstom et. al	Rao & Rubin	Rao & Rubin	Chen et. al	Chen et. al	Chen et. al	Singh et al	Gibbins et al	Range		Gibbins et al	Gibbins et al	Chen, et.al
	2000	2001	2002	2002	2003	2003	2003	2003	2005	min	max	2005	2006	2003
	AMINE SYSTEM RETROFITS TO EXISTING BOILERS											REPOWERING + CO_2 CAPTURE		
Reference Plant (w/o capture)		*	*	*	*	*	*							
Boiler type (subcritical, super, ultra)	sub	sub	sub	sub	sub	sub	sub		sub			super	super	sub
Coal type (bit, subbit, lig) and %S	subbit, 0.5%	bit, 2.7%S	subbit, 0.5%	subbit, 0.5%	subbit, 1.1%S	subbit, 1.1%S	subbit, 1.1%S	subbit						
Emission control technologies (SO_2/NO_x)	none	FGD	none	FGD	FGD	FGD	FGD	not reported	not reported			not reported	not reported	FGD
Reference plant size (MW)	292	434	470	470	248	248	248	400		**248**	**470**			248
Plant capacity factor (%)	80	67	75	75	80	76 (Capture= 80)	76 (Capture=80)	91.3	80	**67**	**91**	80	80	80
Net plant efficiency, LHV (%)	36.2	36.2	36.6		33.1	33.1	33.1		36.0	**33**	**37**	43.5	43.5	
Coal cost, LHV (US$/GJ)	0.98	*1.30*	*1.25*	*1.25*	*1.20*	*1.20*	*1.20*		3.07	**0.98**	**3.07**	3.07	3.07	*1.20*
Reference plant emission rate (t CO_2/MWh)	0.901	0.908	0.941	0.95	1.004	1.004	1.004	0.925		**0.90**	**1.00**			1.004
Capture Plant Design														
CO_2 capture technology	MEA	MEA	MEA	MEA	MEA	MEA	MEA	MEA	MEA			MEA	KS	Selexol
Other equipment included	new FGD	FGD upgrade	New FGD	FGD upgrade	FGD upgrade	FGD upgrade	FGD upgrade	FGD				Advanced supercrit boiler retrofit	Advanced supercrit boiler retrofit	IGCC (Texaco Q) repower +current steam turbine
Net plant size with capture (MW)	294	255	275	275	140	282	282	400		**140**	**400**			590
Auxilary boiler/fuel used? (type, LHV cost)	NG. $4.51/GJ	none	none	none	none	*NG. $2.59/GJ*	*NG. $5.06/GJ*	NG. $3.79/GJ	none			none	none	none
Net plant efficiency, LHV (%)	25.3	21.3	21.4	21.4	18.7				24.0	**19**	**25**	31.5	34.5	32.6
CO_2 capture system efficiency (%)	90	96	90	90	90	90	90	90		**90**	**96**			90
CO_2 emission rate after capture (t/MWh)	0.113	0.059	0.155	0.16	0.177	0.369	0.369	0.324		**0.06**	**0.37**			0.099
CO_2 captured (Mt/yr)	2.090	2.228			1.480	1.480	1.480	2.664		**1.48**	**2.66**			3.684
CO_2 product pressure (MPa)	13.7	13.9	13.9	13.9	13.9	13.9	13.9		10.0	**10**	**14**	10.0	10.0	14.5
CCS energy reqm't. (% more input/MWh)	43	70	71		77				50	**43**	**77**	38	26	
CO_2 reduction per kWh (%)	**87**	**94**	**84**	**83**	**82**	**63**	**63**	**65**		**63**	**94**			
Cost Results	**							**						
Cost year basis (constant dollars)	1999	n/a	2000	2000	2000	2000	2000	2001						
Fixed charge factor (%)	*12.8*	13.0	15.0	15.0	14.8	14.8	14.8	9.4	11.8	**9.4**	**15.0**	11.8	11.8	15
Reference plant TCR (US$/kW)	*112*				0	0	0	0	160	**0**	**160**	480	480	0
Capture plant TCR (US$/kW)	*1059*	1941			837	647	654	*846*	1028	**647**	**1941**	1282	1170	1493
Incremental TCR for capture (US$/kW)	*947*	1602			837	647	654	*846*	868	**647**	**1602**	802	690	1493
Reference plant COE (US$/MWh)	**18.8**		**18.0**	**18.0**	**20.6**	**20.6**	**20.6**		**26.0**	**18**	**26**	**27.0**	**27.0**	**21**
Capture plant COE (US$/MWh)	**54.3**		**70.4**	**66.7**	**66.8**	**51.1**	**62.2**		**65.0**	**51**	**70**	**58.0**	**53.0**	**62.2**
Incremental COE for capture (US$/MWh)	**35.5**	**61.7**	**52.4**	**48.7**	**46.2**	**30.6**	**41.7**	**33.2**	**39.0**	**31**	**62**	**31.0**	**26.0**	**41.2**
% increase in capital cost (over ref. plant)														
% increase in COE (over ref. plant)	**189**		**291**	**271**	**225**	**149**	**203**		**150**	**149**	**291**	**115**	**96**	**196**
Cost of CO_2 captured (US$/t CO_2)	35	42			31	41	56	40		**31**	**56**			
Cost of CO_2 avoided (US$/t CO_2)	45	73	67	59	56	48	66	55		**45**	**73**			46
Capture Cost Confidence Level (see Table 3.6)	- moderate -											- moderate -		

Notes: All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. Values in italics were adjusted from original reported values as explained below. ** Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal and 0.90 for natural gas. **Reported capital costs increased by 15% to estimate interest during construction and other owners' costs.*

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Table 3.9. CO_2 Capture Costs: Natural Gas-Fired Power Plants using Current Technology.

Study Assumptions and Results	**EPRI**	**NETL**	**IEA GHG**	**IEA GHG**	**CCP**	**Rubin et.al**	**Rubin et.al**	**Range**	
	2002	**2002**	**2004**	**2004**	**2005**	**2005**	**2005**	**min**	**max**
Reference Plant (w/o capture)	*					*	*		
Plant type (boiler, gas turbine, comb.cycle)	comb.cycle	comb.cycle	comb.cycle	comb.cycle	comb.cycle	comb.cycle	comb.cycle		
Reference plant size (MW)	509	379	776	776	392	507	507	**379**	**776**
Plant capacity factor (%)	65	85	85	85	95	75	50	**50**	**95**
Net plant efficiency, LHV (%)	*55.1*	57.9	55.6	55.6	57.6	*55.8*	*55.8*	**55**	**58**
Fuel cost, LHV ($/GJ)	*2.82*	3.55	3.00	3.00	*2.96*	*4.44*	*4.44*	**2.82**	**4.44**
Reference plant emission rate (t CO_2/MWh)	0.364	0.344	0.379	0.379	0.37	0.367	0.367	**0.344**	**0.379**
Capture Plant Design									
CO_2 capture technology	MEA	MEA	MEA	KS-1	MEA	MEA	MEA		
Net plant size with capture (MW)	399	327	662	692	323	432	432	**323**	**692**
Net plant efficiency, LHV (%)	*47.4*	49.9	47.4	49.6	47.4	*47.6*	*47.6*	**47**	**50**
CO_2 capture system efficiency (%)	90	90	85	85	86	90	90	**85**	**90**
CO_2 emission rate after capture (t/MWh)	0.045	0.040	0.066	0.063	0.063	0.043	0.043	**0.040**	**0.066**
CO_2 captured (Mt/yr)	0.949	0.875	1.844	1.844	1.09	1.099	0.733	**0.733**	**1.844**
CO_2 product pressure (MPa)	8.4	10.3	11.0	11.0		13.7	13.7	**8**	**14**
CCS energy reqm't. (% more input/MWh)	16	16	15	11	22	17	17	**11**	**22**
CO_2 reduction per kWh (%)	**88**	**88**	**83**	**83**	**83**	**88**	**88**	**83**	**88**
Cost Results									
Cost year basis (constant dollars)	2000	2002	2004	2004		2001	2001		
Fixed charge factor (%)			11.0	11.0	11.0	14.8	14.8	**11.0**	**14.8**
Reference plant TCR (US$/kW)	549	515	539	539	724	554	554	**515**	**724**
Capture plant TCR (US$/kW)	1099	911	938	958	1261	909	909	**909**	**1261**
Incremental TCR for capture (US$/kW)	550	396	399	419	537	355	355	**355**	**550**
Reference plant COE (US$/MWh)	**34.2**	**34.7**	**31.3**	**31.3**	34.2	**43.1**	**50**	**31**	**50**
Capture plant COE (US$/MWh)	**57.9**	**48.3**	**44**	**43.1**	51.8	**58.9**	**72**	**43**	**72**
Incremental COE for capture (US$/MWh)	**23.7**	**13.6**	**12.7**	**11.8**	**17.6**	**15.8**	**22**	**12**	**24**
% increase in capital cost (over ref. plant)	100	77	74	78	74	64	64	**64**	**100**
% increase in COE (over ref. plant)	**69**	**39**	**41**	**38**	51	**37**	**44**	**37**	**69**
Cost of CO_2 captured ($/t CO_2)	57	38	34	33	46	41	57	**33**	**57**
Cost of CO_2 avoided ($/t CO_2)	74	45	41	37	57	49	68	**37**	**74**
Capture Cost Confidence Level (see Table 3.6)	- moderate -								

Notes: All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. Values in italics were adjusted from original reported values as explained below.
** Reported HHV values converted to LHV assuming LHV/HHV = 0.90 for natural gas.*

Table 3.10. CO_2 Capture Costs: New IGCC Power Plants using Current Technology.

Study Assumptions and Results	NETL	NETL	NETL	Parsons	Simbeck	Nsakala, et al	IEA GHG	IEA GHG	IEA GHG	Rubin et al	Rubin et al	Range		Stobbs	Stobbs	Stobbs	IEA GHG
	2002	2002	2002	2002b	2002	2003	2003	2003	2003	2005	2005	min	max	2005	2005	2005	2000
	PLANTS WITH BITUMINOUS COAL FEEDSTOCK													PLANTS WITH OTHER FEEDSTOCKS			
Reference Plant (w/o capture)	*	*	*	*		*											
Gasifier name or type	Shell, O_2 blown, CGCU	E-gas, O_2 blown, CGUC	Texaco quench, O_2 blown	E-gas, O_2 blown	Texaco quench, O_2 blown	Texaco syngas cooler, O_2 blown	Texaco quench, O_2 blown	Texaco quench, O_2 blown	Shell, O_2 blown	Texaco quench, O_2 blown	Texaco quench, O_2 blown				Texaco quench, O_2 blown	Shell, O_2 blown	O_2 blown, partial oxidation
Fuel type (bit, subbit, lig; other) and %S	Illinois #6	Illinois #6	Illinois #6	bit, 2.5% S	bit, 1% S	bit	bit, 1%S	bit, 1%S	bit, 1%S	bit, 2.1%S	bit, 2.1%S			bit	sub-bit	lignite	Natural gas
Reference plant size (MW)	413	401	571	425	521		827	827	776	527	527	**401**	**827**	*[No IGCC Reference Plants]*			790
Plant capacity factor (%)	85	85	65	65	80	80	85	85	85	75	65	**65**	**85**	90	90	90	90
Net plant efficiency, LHV (%)	47.4	46.7	*39.1*	44.8	44.6		38.0	38.0	43.1	39.1	39.1	**38**	**47**				56.2
Fuel cost, LHV (US$/GJ)	*1.03*	*1.03*	*1.28*	1.29	0.98	*1.23*	1.50	1.50	1.50	1.25	1.25	**0.98**	**1.50**	1.90	0.48	0.88	2.00
Reference plant emission rate (tCO2/MWh)	0.682	0.692	0.846	0.718	0.725		0.833	0.833	0.763	0.817	0.817	**0.68**	**0.85**				0.370
Capture Plant Design																	
CO_2 capture technology	Selexol	Selexol	Selexol	Selexol	Selexol	Selexol	Selexol	Selexol. NS	Selexol	Selexol	Selexol			Selexol	Selexol	Selexol	Selexol
Net plant size, with capture (MW)	351	359	457	404	455		730	742	676	492	492	**351**	**742**	445	437	361	820
Net plant efficiency, LHV (%)	40.1	40.1	*31.3*	38.5	39.0	31.5	31.5	32.0	34.5	33.8	33.8	**31**	**40**	32.8	27.0	28.3	48.3
CO_2 capture system efficiency (%)	89.2	87.0	89.0	91.0	91.2		85	85	85	90	90	**85**	**91**	87	92	86	85
CO_2 emission rate after capture (t/MWh)	0.087	0.105	0.116	0.073	0.065	0.104	0.152	0.151	0.142	0.097	0.097	**0.07**	**0.15**	0.130	0.102	0.182	0.065
CO_2 captured (Mt/yr)	1.803	1.870	2.368	1.379	2.151		4.682	4.728	4.050	2.749	2.383	**1.38**	**4.73**	3.049	4.040	3.183	2.356
CO_2 product pressure (MPa)	14.5	14.5	8.3	8.3			11.0	11.0	11.0	13.7	13.7	**8**	**14**	13.9	13.9	13.9	11.0
CCS energy reqm't. (% more input/MWh)	18	16	25	16	14		21	19	25	16	16	**14**	**25**				14
CO_2 reduction per kWh (%)	**87**	**85**	**86**	**90**	**91**		**82**	**82**	**81**	**88**	**88**	**81**	**91**				**82**
Cost Results							**	**	**					***	***	***	**
Cost year basis (constant dollars)	2002	2002	2002	2000	2000		2002	2002	2002	2001	2001			2003	2003	2003	2000
Fixed charge factor (%)	14.8	14.8	15.0	13.8	13.0		11.0	11.0	11.0	14.8	17.3	**11**	**17**				11.0
Reference plant TCR (US$/kW)	1370	1374	1169	1251	1486	1565	*1187*	*1187*	*1371*	1311	1311	**1169**	**1565**				447
Capture plant TCR (US$/kW)	2270	1897	1549	1844	2067	2179	*1495*	*1414*	*1860*	1748	1748	**1414**	**2270**	*2205*	*2518*	*3247*	*978*
Incremental TCR for capture (US$/kW)	900	523	380	593	581	614	*308*	*227*	*489*	437	437	**227**	**900**				*531*
Reference plant COE (US$/MWh)	**40.6**	**40.9**	**43.4**	**47.7**	**43.0**	**53.0**	**45.0**	**45.0**	**48.0**	**48.3**	**61**	**41**	**61**				**21.6**
Capture plant COE (US$/MWh)	**62.9**	**54.4**	**59.9**	**65.8**	**57.7**	**71.5**	**56.0**	**54.0**	**63.0**	**62.6**	**79**	**54**	**79**	68.4	62.1	83.9	**34.4**
Incremental COE for capture (US$/MWh)	**22.3**	**13.5**	**16.5**	**18.1**	**14.7**	**18.5**	**11**	**9**	**15**	**14.3**	**18.2**	**9**	**22**				**12.8**
% increase in capital cost (over ref. plant)	66	38	33	47	39	39	26	19	36	33	33	**19**	**66**				119
% increase in COE (over ref. plant)	55	33	38	38	34	**35**	**24**	**20**	**31**	30	30	**20**	**55**				**59**
Cost of CO_2 captured (US$/t CO_2)	32	19	18	30	21		13	11	19	17	21	**11**	**32**				35
Cost of CO_2 avoided (US$/t CO_2)	37	23	23	28	22	23	16	13	24	20	25	**13**	**37**	31	33	56	42
Capture Cost Confidence Level (see Table 3.6)	- moderate -													- moderate -			moderate

Notes: All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. Values in italics were adjusted from original reported values as explained below. * *Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal.* ** *Reported capital costs increased by 8% to include interest during construction.* ***Reported capital costs increased by 15% to estimate interest during construction and other owners' costs.*

Table 3.11. CO_2 Capture Costs: Hydrogen and Multi-product Plants using Current or Near-commercial Technology. *(continued on next page)*

	HYDROGEN AND ELECTRICITY PRODUCTS								
Study Assumptions and Results	**Simbeck**	**NRC**	**NRC**	**Parsons**	**Mitretek**	**Kreutz, et al**	**Kreutz, et al**	**Range**	
	2004	**2004**	**2004**	**2002a**	**2003**	**2005**	**2005**	**min**	**max**
Reference Plant (w/o capture)	*			*	*				
Plant products (primary/secondary)	H_2	H_2	H_2	H_2+electricity	H_2+electricity	H_2+electricity	H_2+electricity		
Production process or type	Steam reforming	Steam reforming	Texaco quench, CGCU	Conv E-Gas, CGCU, H_2SO_4 coproduct	Texaco quench, CGCU, Claus/Scot sulfur coproduct	Texaco quench	Texaco quench		
Feedstock	Natural gas	Natural gas	Coal	Pgh #8 Coal	Coal	Coal	Coal		
Feedstock cost, LHV ($/GJ)	*5,26*	4,73	1,20	*0,89*	*1,03*	1,26	1,26	**0.89**	**5.26**
Ref plant input capacity, LHV (GJ/hr)	*9848*	7235	8861	*2627*	*2954*	6706	6706	**2627**	**9848**
Ref plant output capacity, LHV: Fuels (GJ/hr)	*7504*	5513	6004	*1419*	*1579*	3853	3853	**1419**	**7504**
Electricity (MW)	-44	-32	-121	38	20	78	78	**-121**	**78**
Net plant efficiency, LHV (%)	74,6	74,6	62,9	59,2	55,9	61,7	61,7	**55.9**	**74.6**
Plant capacity factor (%)	90	90	90	80	85	80	80	**80**	**90**
CO_2 emitted (Mt CO_2/yr)	4,693	3,339	7,399	1,795	2,148	4,215	4,215	**1.80**	**7.40**
Carbon exported in fuels (MtC/yr)	0	0	0	0	0	0	0	**0**	**0**
Total carbon released (kg CO_2/GJ products)	81	78	168	164	174	145	145	**78**	**174**
Capture Plant Design									
CO_2 capture/separation technology	Amine scrubber, SMR flue gas	MEA scrubber	Not reported	Selexol	Not reported	Selexol	CO_2 H_2S co-capture, Selexol		
Capture plant input capacity, LHV (GJ/hr)	*11495*	8339	8861	*2627*	*2954*	6706	6706	**2627**	**11495**
Capture plant output capacity, LHV: Fuels (GJ/hr)	*7504*	6004	6004	*1443*	*1434*	3853	3853	**1434**	**7504**
Electricity (MW)	-129	-91	-187	12	27	39	35	**-187**	**39**
Net plant efficiency, LHV (%)	61.2	68.1	60.2	56.6	51.8	59.5	59.3	**51.8**	**68.1**
CO_2 capture efficiency (%)**	90	90	90	92	87	91	95	**87**	**95**
CO_2 emitted (Mt CO_2/yr)***	1.280	0.604	1.181	0.143	0.279	0.338	0.182	**0.14**	**1.280**
Carbon exported in fuels (Mt C/yr)	0	0	0	0	0	0	0	**0.00**	**0**
Total carbon released (kg CO_2/GJ products)	23.0	13.5	28.1	13.7	24.5	12.1	6.5	**6.5**	**28.1**
CO_2 captured (Mt CO_2/yr)	4.658	3.378	6.385	1.654	1.869	3.882	4.037	**1.7**	**6.4**
CO_2 product pressure (MPa)	13.7	13.7	13.7	13.4	20	15	15	**13.4**	**20.0**
CCS energy reqm't. (% more input/GJ plant output)	21.8	9.5	4.5	4.7	7.9	3.6	3.9	**3.6**	**21.8**
CO_2 reduction per unit product (%	**72**	**83**	**83**	**92**	**86**	**92**	**96**	**72**	**96**
Cost Results									
Cost year basis (constant dollars)	2003	2000	2000	2000	2000	2002	2002		
Fixed charge rate (%)	20.0	16.0	16.0	14.3	13.0	15.0	15.0	**13.0**	**20.0**
Reference plant TCR (million US$)****	*668*	*469*	*1192*	*357*	*365*	*887*	*887*	**357**	**1192**
Capture plant TCR (million US$)****	*1029*	*646*	*1218*	*415*	*409*	*935*	*872*	**409**	**1218**
% increase in capital cost (%)	54.1	37.7	2.2	16.5	11.9	5.4	-1.7	**-1.7**	**54.1**
Ref. plant electricity price (US$/MWh)	50.0	45.0	45.0	30.8	35.6	46.2	46.2	**30.8**	**50.0**
Capture plant electricity price (US$/MWh)	50.0	45.0	45.0	30.8	53.6	62.3	60.5	**30.8**	**62.3**
% increase in assumed electricity price	0.0	0.0	0.0	0.0	50.6	34.8	31.0	**0.0**	**50.6**
Ref. plant fuel product cost, LHV (US$/GJ)	***10.03***	**8.58**	**7.99**	***6.51***	***7.29***	**7.19**	**7.19**	**6.51**	**10.03**
Capture plant fuel product cost, LHV (US$/GJ)	***13.29***	**10.14**	**8.61**	***7.90***	***8.27***	**7.86**	**7.52**	**7.52**	**13.29**
Increase in fuel product cost (US$/GJ)	**3.26**	**1.56**	**0.62**	**1.38**	**0.98**	**0.67**	**0.32**	**0.32**	**3.26**
% increase in fuel product cost	**32.5**	**18.2**	**7.7**	**21.1**	**13.4**	**9.3**	**4.5**	**4.5**	**32.5**
Cost of CO_2 captured (US$/t CO_2)	38.9	20.7	4.1	8.7	6.0	4.8	2.2	**2.2**	**38.9**
Cost of CO_2 avoided (US$/t CO_2)	56.3	24.1	4.4	9.2	6.5	5.0	2.3	**2.3**	**56.3**
Confidence Level (see Table 3.6)	high		high	- moderate -					

Notes: All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. Values in italics were adjusted from original reported values as explained below. ** Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal, 0.846 for hydrogen, and 0.93 for F-T liquids. **CO_2 capture efficiency = (C in CO_2 captured/stored)/(C in fossil fuel input to plant - C in carbonaceous fuel products of plant)*100; C associated with imported electricity is not included. ***Includes CO_2 emitted in the production of electricity imported by the plant. ****Reported total plant investment values increased by 3.5% to estimate total capital requirement.*

Table 3.11. *Continued.*

	LIQUID FUEL AND ELECTRICITY PRODUCTS										
Study Assumptions and Results	**Mitretek**	**Larson/Ren**	**Larson/Ren**	**Larson/Ren**	**Larson/Ren**	**Celik et al.**	**Celik et al.**	**Celik et al.**	**Celik et al.**	**Range**	
	2001	**2003**	**2003**	**2003**	**2003**	**2005**	**2005**	**2005**	**2005**	**min**	**max**
Reference Plant (w/o capture)	*										
Plant products (primary/secondary)	F-T liquids +electricity	MeOH +electricity	MeOH +electricity	DME +electricity	DME +electricity	DME + electricity	DME + electricity	DME + electricity	DME + electricity		
Production process or type	Unspecified O_2-blown gasifier, unspecified synthesis reactor	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,	Texaco quench, Liquid phase reactor, Once-through config,		
Feedstock	Coal	Coal	Coal	Coal	Coal	Coal	Coal	Coal	Coal		
Feedstock cost, LHV (US$/GJ)	*1,09*	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	**1.00**	**1.09**
Ref plant input capacity, LHV (GJ/hr)	*16136*	9893	9893	8690	8690	7931	7931	7931	7931	**7931**	**16136**
Ref plant output capacity, LHV: Fuels (GJ/hr)	*7161*	2254	2254	2160	2160	2161	2161	2161	2161	**2160**	**7161**
Electricity (MW)	697	625	625	552	552	490	490	490	490	**490**	**697**
Net plant efficiency, LHV (%)	59.9	45.5	45.5	47.7	47.7	49.5	49.5	49.5	49.5	**45.5**	**59.9**
Plant capacity factor (%)	90	85	85	85	85	80	80	80	80	**80**	**90**
CO_2 emitted (Mt CO_2/yr)	8.067	5.646	5.646	4.895	4.895	4.077	4.077	4.077	4.077	**4.08**	**8.07**
Carbon exported in fuels (Mt C/yr)	1.190	0.317	0.317	0.334	0.334	0.274	0.274	0.274	0.274	**0.27**	**1.19**
Total carbon released (kg CO_2/GJ products)	163	203	203	198	198	185	185	185	185	**163**	**203**
Capture Plant Design											
CO_2 capture/separation technology	Amine scrubber	Selexol	CO_2 H_2S cocapture. Selexol	Selexol	CO_2 H_2S cocapture. Selexol	CO_2 H_2S cocapture. Rectisol	CO_2 H_2S cocapture. Rectisol	CO_2 H_2S cocapture. Rectisol	CO_2 H_2S cocapture. Rectisol		
Capture plant input capacity, LHV (GJ/hr)	*16136*	9893	9893	8690	Coal	7931	7931	7931	7931	**7931**	**16136**
Capture plant output capacity LHV: Fuels (GJ/hr)	*7242*	2254	2254	2160	2160	2161	2160	2160	2160	**2160**	**7242**
Electricity (MW)	510	582	577	531	527	469	367	365	353	**353**	**582**
Net plant efficiency, LHV (%)	56.3	44.0	43.8	46.9		48.5	43.9	43.8	43.2	**43**	**56**
CO_2 capture efficiency (%)**	91	58	63	32	37	36	89	92	97	**32**	**97**
CO_2 emitted (Mt CO_2/yr)***	0.733	2.377	2.099	3.320	3.076	2.598	0.390	0.288	0.028	**0.03**	**3.32**
Carbon exported in fuels (Mt C/yr)	1.2	0.317	0.317	0.294	0.294	0.274	0.274	0.274	0.274	**0.274**	**1.200**
Total carbon released (kg CO_2/GJ products)	71.7	109.2	101.0	144.9	137.4	134	57	53	43	**43**	**145**
CO_2 captured (MtCO_2/yr)	7.260	3.269	3.547	1.574	1.819	1.479	3.692	3.790	4.021	**1.48**	**7.26**
CO_2 product pressure (MPa)	13.8	15	15	15	15	15	15	15	15	**14**	**15**
CCS energy reqm't. (% more input/GJ plant output)	6.5	3.6	4.0	1.9		2.0	12.8	13.0	14.5	**1.9**	**14.5**
CO_2 reduction per unit product (%	**56**	**46**	**50**	**27**	**31**					**27**	**56**
Cost Results											
Cost year basis (constant dollars)						2003	2003	2003	2003		
Fixed charge rate (%)	12.7	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	**12.7**	**15.0**
Reference plant TCR (million US$)****	*2160*	*1351*	*1351*	*1215*	*1215*	*1161*	*1161*	*1161*	*1161*	**1161**	**2160**
Capture plant TCR (million US$)****	*2243*	*1385*	*1220*	*1237*	*1090*	*1066*	*1128*	*1164*	*1172*	**1066**	**2243**
% increase in capital cost (%)	3.8	2.6	-9.7	1.8	-10.3	-8.1	-2.8	0.2	0.9	**-10.3**	**3.8**
Ref. plant electricity price (US$/MWI	35.6	42.9	42.9	42.9	42.9	44.1	44.1	44.1	44.1	**35.6**	**44.1**
Capture plant electricity price (US$/MWh)	53.6	42.9	42.9	42.9	42.9	58.0	58.0	58.0	58.0	**42.9**	**58.0**
% increase in assumed electricity pric	50.5	0.0	0.0	0.0	0.0	31.5	31.5	31.5	31.5	**0.0**	**50.5**
Ref. plant fuel product cost, LHV (US$/GJ)	***5.58***	**9.12**	**9.12**	**8.68**	**8.68**	**7.41**	**7.41**	**7.41**	**7.41**	**5.6**	**9.1**
Capture plant fuel product cost, LH (US$/GJ)	***5.43***	**10.36**	**8.42**	**9.37**	**7.57**	**6.73**	**7.18**	**7.65**	**8.09**	**5.4**	**10.4**
Increase in fuel product cost (US$/GJ)	**-0.15**	**1.24**	**-0.70**	**0.69**	**-1.11**	**-0.68**	**-0.23**	**0.24**	**0.68**	**-1.1**	**1.2**
% increase in fuel product cost	**-5.7**	**13.6**	**-7.7**	**7.9**	**-12.8**	**-9.2**	**-3.1**	**3.2**	**9.2**	**-12.8**	**13.6**
Cost of CO_2 captured (US$/t CO_2)		12.3	-6.4	13.3	-18.4	-12.4	-1.5	1.5	4.1	**-18.4**	**13.3**
Cost of CO_2 avoided (US$/t CO_2)		13.2	-6.9	13.0	-18.3	-13.3	-1.8	1.8	4.8	**-18.3**	**13.2**
Confidence Level (see Table 3.6)	moderate	moderate	moderate	- low to moderate -							

Notes: All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. Values in italics were adjusted from original reported values as explained below. ** Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal, 0.846 for hydrogen, and 0.93 for F-T liquids. **CO_2 capture efficiency = (C in CO_2 captured/stored)/(C in fossil fuel input to plant - C in carbonaceous fuel products of plant)*100; C associated with imported electricity is not included. ***Includes CO_2 emitted in the production of electricity imported by the plant. ****Reported total plant investment values increased by 3.5% to estimate total capital requirement.*

Table 3.12. Capture Costs: Other Industrial Processes using Current or Advanced Technology.

	CURRENT TECHNOLOGY									ADVANCED TECHNOLOGY			
Study Assumptions and Cost Results	**Farla**	**IEA GHG**	**IEA GHG**	**IEA GHG**	**Möllersten**	**Möllersten**	**Möllersten**	**CCP**	**CCP**	**CCP**	**CCP**	**CCP**	**CCP**
	1995	**2000**	**2000**	**2002**	**2003**	**2003**	**2003**	**2005**	**2005**	**2005**	**2005**	**2005**	**2005**
Reference Plant (w/o capture)													
Industrial process	Iron production	Oil refining petrochemical	Oil refining petrochemical	High purity CO_2 sources	Pulp mill	Pulp mill	Ethanol fermentation	Refinery heaters & boilers	Small gas turbines	Refinery heaters & boilers	Refinery heaters & boilers	Small gas turbines	Small gas turbines
Feedstock type	Coke	Refinery gas / natural gas	Refinery gas / natural gas		Black liquor and bark	Black liquor	Sugar cane	Mixed	NG	Mixed	Mixed	natural gas	natural gas
Plant size (specify units)	168 kg/s iron	315 kg/s crude oil	315 kg/s crude oil		17.9 kg/s pulp	17.9 kg/s pulp	9.1 kg/s ethanol	1351	358	1351	1351	358	358
Plant capacity factor (%)	95.3	90	90	90	90.4	90.4	49.3	90.4	98.5	90.4	90.4	98.5	98.5
Feedstock cost (US$/unit specified)					$3/GJ LHV	$3/GJ LHV							
Ref. plant emission rate (kg CO_2/unit product)								*2.96*	*2.96*	*2.96*	*2.96*	*2.96*	*2.96*
Capture Plant Design								0.22	0.82	0.22	0.22	0.82	0.82
CO_2 capture/separation technology	MDEA	MEA	Pre-combustion	Compression only	Amine	Physical solvent							
Location of CO_2 capture	Blast furnace gas	Fired heaters and H_2 plant	Fired heaters and H_2 plant		Boiler	IGCC	Fermentation and bagasse boiler	MEA Baseline (postcomb)	MEA Baseline (postcomb)	Membrane Water Gas Shift w/ DOE-membrane. GRACE (precomb)	FlueGas Recycle & ITM (oxyfuel)	Very Large Scale ATR (precomb)	Sorption Enhanced Water Gas Shift (precomb)
Capture unit size (specify units)					392 MW fuel	338 MW fuel		1351	358	1351	1351	358	358
CO_2 capture system efficiency (%)	90	95	91		90	90	100 / 90						
Energy source(s) for capture (type +onsite vs. offsite)													
Are all energy-related CO_2 emissions included?								0.09	0.19	0.09	0.05	0.10	0.14
CO_2 emission rate after capture (kg CO_2/unit product)								2.19	1.90	1.99	2.09	2.88	2.50
CO_2 captured (Mt/yr)	2.795	1.013	1.175	1.970	0.969	0.399	0.560						
CO_2 product pressure (MPa)	11.0	11.0	11.0	8.0	10.0	10.0	10.0						
CO_2 reduction per unit of product (%)								**60.3**	**76.5**	**58.4**	**75.8**	**87.4**	**82.2**
Cost Results													
Cost year basis (constant dollars)													
Fixed charge factor (%)					15	15	15	11.0	11.0	11.0	11.0	11.0	11.0
Ref. plant capital cost (US$/unit capacity)													
Capture plant capital cost (US$/unit capacity)													
Incremental capital cost (MUS$ per kg/s CO_2)*	3.8	4.1	4.9	0.3	3.2	1.9	2.6	0	0	0	0	0	0
Ref. plant cost of product (US$/unit)								0.0	0.0	0.0	0.0	0.0	0.0
Capture plant cost of product (US$/unit)								10.2	55.1	6.1	6.8	54.2	48.2
Incremental cost of product (US$/unit)								**10.2**	**55.1**	**6.1**	**6.8**	**54.2**	**48.2**
% increase in capital cost (over ref. plant)													
% increase in unit cost of product (over ref. plant)													
Cost of CO_2 captured (US$/t CO_2)		50	60					55.3	90.9	36.4	38.2	59.0	60.5
Cost of CO_2 avoided (US$/t CO_2)	35	74	116	10	34	23	53	78.1	88.2	48.1	41.0	76.0	71.8
Capture Cost Confidence Level (see Table 3.6)	- moderate -									- low -			

Notes: All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. Values in italics were adjusted from original reported values as explained below.

*Capital costs are incremental costs of capture, excluding cost of make-up steam and power generation, and also excluding interest during construction and other owner's costs.

Table 3.13. Capture Costs: Advanced Technologies for Electric Power Plants. *(continued on next page)*

	OXYFUEL COMBUSTION								ADVANCED PC	
Study Assumptions and Results	**Alstom, et. al**	**Singh et. al**	**Stobbs**	**Dillon et.al**	**Nsakala, et.al**	**Nsakala, et.al**	**Nsakala, et.al**		**Gibbins et.al**	**Gibbins et.al**
	2001	**2003**	**2005**	**2005**	**2003**	**2003**	**2003**		**2005**	**2005**
Reference Plant (w/o capture)	*				*	*	*			
Power plant type	RETROFIT subcrit PC	RETROFIT PC + aux NGCC	RETROFIT PC	New PC	Air-fired CFB	Air-fired CFB	Air-fired CFB			
Fuel type (bit, subbit, lig; NG, other) and %S	bit, 2.7%S	subbit	lignite	bit	bit, 2.3%S	bit, 2.3%S	bit, 2.3%S			
Reference plant net size (MW)	434	400	300	677	193	193	193			
Plant capacity factor (%)	67	91		85	80	80	80		85	85
Net plant efficiency, LHV (%)				44.2	*37.0*	*37.0*	*37.0*		45,6	45,6
Fuel cost, LHV (US$/GJ)	*1.30*			1.50	*1.23*	*1.23*	*1.23*		1,50	1,50
Reference plant emission rate (t CO_2/MWh)	0.908	0.925	0.883	0.722	0.909	0.909	0.909			
Capture Plant Design										
CO_2 capture technology	oxyfuel	oxyfuel	oxyfuel	oxyfuel	oxyfuel	oxyfuel w/ CMB	chemical looping w/CMB			
Net plant size with capture (MW)	273	400		532	135	197	165			
Net plant efficiency, LHV (%)	*23.4*			35.4	*25.8*	*31.3*	*32.2*		34,3	36,5
CO_2 capture system efficiency (%)				*~91*						
CO_2 emission rate after capture (t/MWh)		0.238	0.145	0.085	0.086	0.073	0.005			
CO_2 captured (Mt/yr)		2.664								
CO_2 product pressure (MPa)	13.9	15	13.7	11					11,0	11,0
CCS energy reqm't. (% more input/MWh)				25	43	18	15		33	25
CO_2 reduction per kWh (%)		**74**		**88.2**	**90.5**	**92.0**	**99.5**			
Cost Results	**	**								
Cost year basis (constant dollars)		2001	2000		2003	2003	2003			
Fixed charge factor (%)	13.0	9.4		*11*					*11,0*	*11,0*
Reference plant TCR (US$/kW)		0		1260	1500	1500	1500		1022	1022
Capture plant TCR (US$/kW)	*1527*	*909*	*4570*	1857	2853	2731	1912		1784	1678
Incremental TCR for capture (US$/kW)	*1198*	*909*		597	1354	1232	413		762	656
Reference plant COE (US$/MWh)			**44.5**	**44**	**45.3**	**45.3**	**45.3**		**37**	**37**
Capture plant COE (US$/MWh)			**97.5**	**61.2**	**82.5**	**70.5**	**58.4**		**61**	**57**
Incremental COE for capture (US$/MWh)	44.5	23.9	53	17.2	37.2	25.2	13.1		24	20
% increase in capital cost (over ref. plant)				47	90	82	28		75	64
% increase in COE (over ref. plant)			**119**	**39**	**82**	**56**	**29**		**65**	**54**
Cost of CO_2 captured (US$/t CO_2)		29								
Cost of CO_2 avoided (US$/t CO_2)	54	35	*72*	27	45	30	14			
Capture Cost Confidence Level (see Table 3.6)	- low -					very low	very low			

Notes: All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. Values in italics were adjusted from original reported values as explained below.
***Reported value increased by 15% to estimate interest during construction and other owners' costs.*

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Table 3.13. *Continued.*

	ADVANCED NGCC								ADVANCED IGCC					ADVANCED HYBRIDS	
Study Assumptions and Results	**Simbeck**	**Parsons**	**Parsons**	**CCP**	**CCP**	**CCP**	**CCP**	**Dillon et.al**	**Parsons**	**NETL**	**NETL**	**CCP**	**CCP**	**NETL**	**Parsons**
	2002	**2002b**	**2002b**	**2005**	**2005**	**2005**	**2005**	**2005**	**2002b**	**2002**	**2002**	**2005**	**2005**	**2002**	**2002b**
Reference Plant (w/o capture)									*	*	*			*	
Power plant type	comb.cycle H-class turbine	comb.cycle H-class turbine	comb.cycle H-class turbine					NGCC	E-gas, O_2, water scrubber; H-class turbine	E-gas, O_2, CGCU, Hydraulic air compression	E-gas, O_2, CGCU, Hydraulic air compression w/ open loop water system	Canada coke gasification	Canada coke gasification		CHAT SOFC
Fuel type (bit, subbit, lig; NG, other) and %S	Nat. gas	Nat. gas	Nat. gas	NG	NG	NG	NG	NG	Illinois #6	Illinois #6	Illinois #6	Coke	Coke	Illinois #6	Nat.gas
Reference plant net size (MW)	480	384	384	392	392	392	507	388	425	326	408	588	588	644	557
Plant capacity factor (%)	80	65	80	95	95	95	95	85	80	85	85	91.3	91.3	85	80
Net plant efficiency, LHV (%)	60.0	59.5	59.5	57.6 %	57.6 %	57.6 %	57.6 %	56.0	41.1	43.8	54.9			56.4	66.2
Fuel cost, LHV (US$/GJ)	4.86	2.82	2.82	*2.96*	*2.96*	*2.96*	*2.96*	3.00	*1.23*	*1.03*	*1.03*	*2.96*	*2.96*	*1.03*	2.82
Reference plant emission rate (t CO_2/MWh)	0.342	0.338	0.338	0.37	0.37	0.37	0.37	0.371	0.720	0.712	0.568	0.95	0.95	0.572	0.302
Capture Plant Design															
CO_2 capture technology	MEA	MEA	MEA	MEA low cost/ CCGT-integrated (postcomb)	Membrane Contactor; KS-1 (postcomb)	Hydrogen Membrane Reformer (precomb)	Sorption Enhanced Water Gas Shift- Air ATR (precomb)	Oxyfuel	Selexol	Selexol		IGCC w/ capture (precomb)	IGCC w/ advanced capture (precomb)		
Net plant size with capture (MW)	413	311	311	345	335	361	424	440	387	312	404	699	734	755	517
Net plant efficiency, LHV (%)	51.7	48.1	48.1	50.6	49.2	53.0	48.2	44.7	33.8	35.2	45.4			49.7	46.1
CO_2 capture system efficiency (%)	85	90	90	86	86	100	90		91.5	92.7	92.7			90	86.8
CO_2 emission rate after capture (t/MWh)	0.06	0.042	0.042	0.06	0.06	0.00	0.04	0.011	0.074	0.065	0.050	0.27	0.28	0.046	0.043
CO_2 captured (Mt/yr)	0.980	0.669	0.823	1.09	1.09	1.27	1.47		2.074	1.984	1.984	6.80	6.44	3.390	
CO_2 product pressure (MPa)	13.7	8.3	8.3					11	8.3	14.5	14.5			14.5	8.3
CCS energy reqm't. (% more input/MWh)	16	24	24	-99	-99	-99	-99	25	22	24	21			13	44
CO_2 reduction per kWh (%)	**82**	**88**	**88**	**84.1**	**83.6**	**100**	**87.9**	**97.0**	**90**	**91**	**91**	**71.2**	**71.1**	**92**	**86**
Cost Results															
Cost year basis (constant dollars)	2001	2000	2000						2000	2002	2002			2002	2000
Fixed charge factor (%)	15.0			11.0	11.0	11.0	11.0	11	15.0	14.8	14.8	11.0	11.0	14.8	
Reference plant TCR (US$/kW)	*582*	539	496	724	724	724	724	559	1249	1436	881.4	1398	1398	1508	623
Capture plant TCR (US$/kW)	*1216*	1026	**943**	1002	1225	1058	1089	1034	1698	2189	1450	1919	1823	1822	
Incremental TCR for capture (US$/kW)	*634*	487	447	278	501	334	365	475	449	753	568	521	425	314	
Reference plant COE (US$/MWh)	**42.9**	**33.5**	**30.7**	34.2	34.2	34.2	34.2	**33.5**	**41.0**	**47.0**	**28.5**	32.3	32.3	**41.1**	
Capture plant COE (US$/MWh)	**65.9**	**54.1**	**48.8**	45.1	48.9	43.2	45.4	**50.3**	**53.6**	**65.5**	**41.8**	42.1	40.5	**48.8**	
Incremental COE for capture (US$/MWh)	23	20.6	18.1	10.9	14.7	9.0	11.2	16.8	12.6	18.5	13.3	9.8	8.2	7.7	
% increase in capital cost (over ref. plant)	109	90	90	38	69	46	50	85	36	52	64	37	30	21	
% increase in COE (over ref. plant)	**54**	**61**	**59**	32	43	26	33	**50**	**31**	**39**	**47**	**30**	**25**	**19**	
Cost of CO_2 captured (US$/t CO_2)		48		30.2	39.5	22.5	28.2		16	22	20	11	10	13	
Cost of CO_2 avoided (US$/t CO_2)	82	70	61	35.1	47.5	24.4	34.4	47	19	29	26	14	12	15	
Capture Cost Confidence Level (see Table 3.6)	- low to moderate -				- low to very low -				- low -					- very low -	

Notes: All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. Values in italics were adjusted from original reported values as explained below.
***Reported value increased by 15% to estimate interest during construction and other owners' costs.*

Table 3.14. CO_2 Capture Costs: Multi-product Plants using Advanced Technology.

Study Assumptions and Results	Simbeck	NRC	NRC	Parsons	Mitretek	Mitretek	Mitretek	Range	
	2004	2004	2004	2002a	2003	2003	2003	min	max
Capture Plant Design	*			*	*	*	*		
Plant products (primary/secondary)	H_2	H_2	H_2	H_2 +electricity	H_2 +electricity	H_2 +electricity	H_2 +electricity		
Production process or type	Autothermal reforming with O_2 provided by ITM	78% eff ATR/SMR, adv CO_2 compressor	Gasifier LHV= 75-->80%, Adv ASU, membrane sep, adv CO_2 compressor	High-pressure E-gas, HGCU,HTMR, H2SO4 coproduct	Advanced E-gas, HGCU, HTMR	Advanced E-gas, HGCU, HTMR, large elect coproduct	Advanced E-gas, HGCU, HTMR, SOFC, large elect coproduct		
Feedstock	Natural gas	Natural gas	Coal	Pgh #8 Coal	Coal	Coal	Coal		
Feedstock cost, LHV ($/GJ)	*5.26*	4.73	1.20	*0.89*	*1.03*	*1.03*	*1.03*	**1**	**5**
Plant capacity factor (%)	90	90	90	80	85	85	85	**80**	**90**
CO_2 capture/separation technology	Oxyfuel	?	?	Oxyfuel	Oxyfuel	Oxyfuel	Oxyfuel		
Capture plant input capacity, LHV (GJ/hr)	*9527*	7697	8121	*2794*	*3020*	*6051*	*6051*	**2794**	**9527**
Capture plant output capacity, LHV: Fuels (GJ/hr)	*7504*	6004	6004	*1956*	*1904*	*1844*	*1808*	**1808**	**7504**
Electricity (MW)	-13	-66	-88	7	25	416	519	**-88**	**519**
Net plant efficiency, LHV (%)	78.3	74.9	70.0	70.9	66.0	55.2	60.7	**55**	**78**
CO_2 capture efficiency (%)**	95	90	90	94	100	100	95	**90**	**100**
CO_2 emitted (Mt CO_2/yr)***	0.086	0.505	0.873	0.117	0.000	0.000	0.191	**0.000**	**0.873**
Carbon exported in fuels (Mt C/yr)	0	0	0	0	0	0	0	**0**	**0**
Total carbon released (kg CO_2/GJ products)	1.46	11.10	19.45	8.45	0.00	0.00	6.96	**0.0**	**19.5**
CO_2 captured (Mt CO_2/yr)	4.074	3.119	5.853	1.855	1.918	3.846	3.652	**1.9**	**5.9**
CO_2 product pressure (MPa)	13.7	13.7	13.7	13.4	20	20	20	**13.4**	**20.0**
Cost Results									
Cost year basis (constant dollars)	2003	2000	2000	2000	2000	2000	2000		
Fixed charge rate (%)	20	16	16	14.3	12.7	12.7	12.7	**12.7**	**20.0**
Capture plant TCR (million US$)****	*725*	*441*	*921*	*398*	*441*	*950*	*1023*	**398**	**1023**
Capture plant electricity price (US$/MWh)	50.0	45.0	45.0	30.8	53.6	53.6	53.6	**31**	**54**
Capture plant fuel product cost, LHV ($/GJ)	*9.84*	8.53	6.39	*5.79*	*6.24*	*3.27*	*1.13*	**1.13**	**9.84**
Capture Cost Confidence Level (see Table 3.6)	low	low	low	- low to very low -			very low		

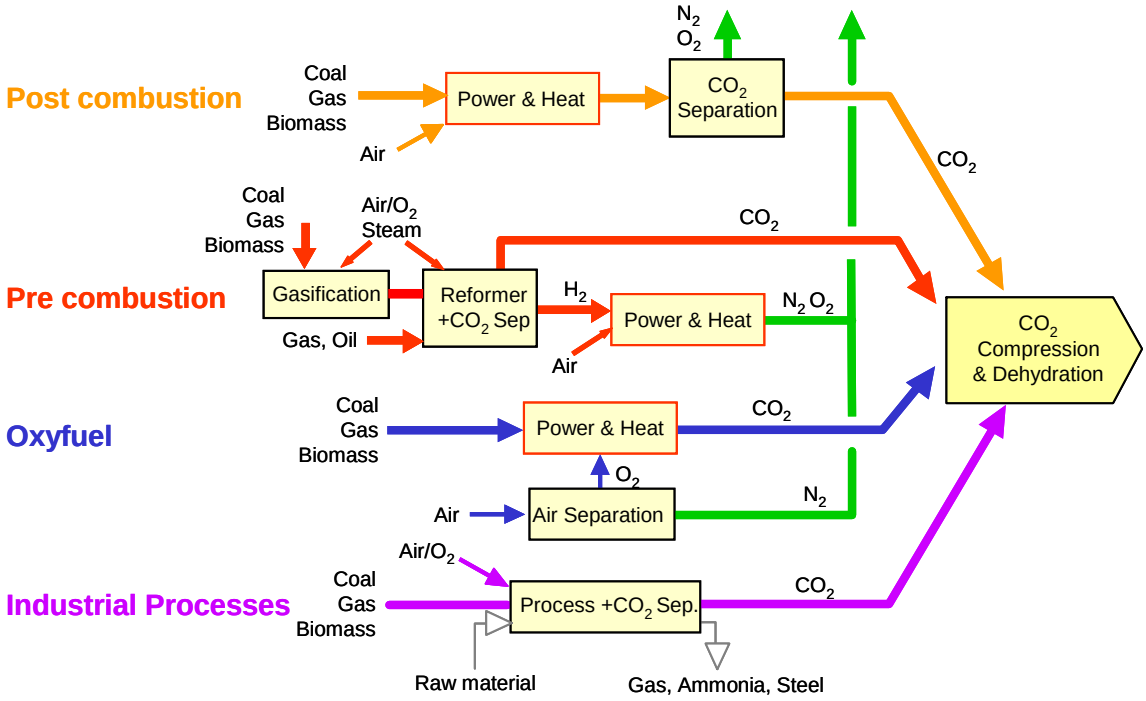
Notes: All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. Values in italics were adjusted from original reported values as explained below.
** Reported HHV values converted to LHV assuming LHV/HHV = 0.96 for coal, and 0.846 for hydrogen. **CO_2 capture efficiency = (C in CO_2 captured/stored)/(C in fossil fuel input to plant - C in carbonaceous fuel products of plant)*100; C associated with imported electricity is not included. ***Includes CO_2 emitted in the production of electricity imported by the plant. ****Reported total plant investment values increased by 3.5% to estimate total capital requirement.*

Table 3.15. Summary of New Plant Performance and CO_2 Capture Cost Based on Current Technology.

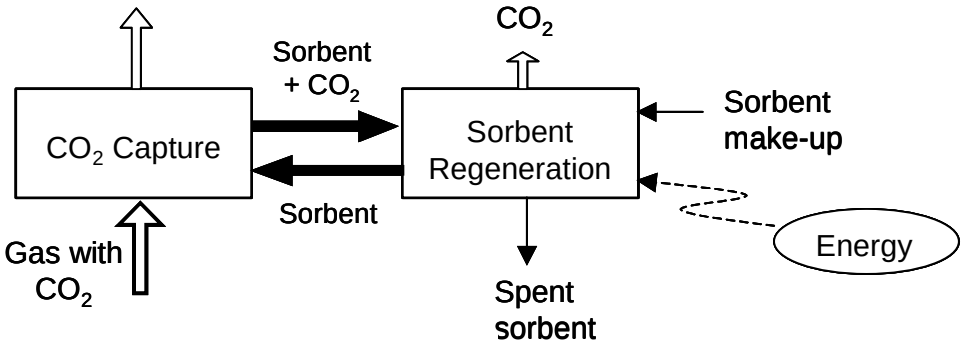
Performance and Cost Measures	New NGCC Plant			New PC Plant			New IGCC Plant			New Hydrogen Plant			(Units for H_2 Plant)
	Range		Rep.	Range		Rep.	Range		Rep.	Range		Rep.	
	low	high	Value	low	high	Value	low	high	Value	low	high	Value	
Emission rate w/o capture (kg CO_2/MWh)	344 - 379		*367*	736 - 811		*762*	682 - 846		*773*	78 - 174		*137*	kg CO_2/GJ (w/o capture)
Emission rate with capture (kg CO_2/MWh)	40 - 66		*52*	92 - 145		*112*	65 - 152		*108*	7 - 28		*17*	kg CO_2/GJ (with capture)
Percent CO_2 reduction per kWh (%)	83 - 88		*86*	81 - 88		*85*	81 - 91		*86*	72 - 96		*86*	% reduction/unit of product
Plant efficiency w/ capture, LHV basis (%)	47 - 50		*48*	30 - 35		*33*	31 - 40		*35*	52 - 68		*60*	Capture plant efficiency (% LHV)
Capture energy reqm't. (% more input/MWh)	11 - 22		*16*	24 - 40		*31*	14 - 25		*19*	4 - 22		*8*	% more energy input/GJ product
Total capital reqm't. w/o capture (US$/kW)	515 - 724		*568*	1161 - 1486		*1286*	1169 - 1565		*1326*	*[No unique normalization for multi-product plants]*			Capital reqm't. w/o capture
Total capital reqm't. with capture (US$/kW)	909 - 1261		*998*	1894 - 2578		*2096*	1414 - 2270		*1825*				Capital reqm't. with capture
Percent increase in capital cost w/ capture (%)	64 - 100		*76*	44 - 74		*63*	19 - 66		*37*	-2 - 54		*18*	% increase in capital cost
COE w/o capture (US$/MWh)	31 - 50		*37*	43 - 52		*46*	41 - 61		*47*	6,5 - 10,0		*7,8*	H_2 cost w/o capture (US$/GJ)
COE with capture only (US$/MWh)	43 - 72		*54*	62 - 86		*73*	54 - 79		*62*	7,5 - 13,3		*9,1*	H_2 cost w/ capture (US$/GJ)
Increase in COE w/ capture (US$/MWh)	12 - 24		*17*	18 - 34		*27*	9 - 22		*16*	0,3 - 3,3		*1,3*	Increase in H_2 cost (US$/GJ)
Percent increase in COE w/ capture (%)	37 - 69		*46*	42 - 66		*57*	20 - 55		*33*	5 - 33		*15*	% increase in H_2 cost
Cost of CO_2 captured (US$/t CO_2)	33 - 57		*44*	23 - 35		*29*	11 - 32		*20*	2 - 39		*12*	US$/t CO_2 captured
Cost of CO_2 avoided (US$/t CO_2)	37 - 74		*53*	29 - 51		*41*	13 - 37		*23*	2 - 56		*15*	US$/t CO_2 avoided
Capture Cost Confidence Level (see Table 3.6)	moderate			moderate			moderate			moderate to high			Confidence Level (see Table 3.6)

Notes: See Section 3.6.1 for calculation of energy requirement for capture plants. Values in italics were adjusted from original reported values as explained below.
[a] Ranges and representative values are based on data from Tables 3.8, 3.11, 3.11 and 3.12. All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs.
[b] All PC and IGCC data are for bituminous coals only at costs of US$1.0-1.5/GJ (LHV); all PC plants are supercritical units. [c] NGCC data based on natural gas prices of US$2.8-4.4/GJ (LHV basis). [d] Cost are in constant US dollars (approx. year 2002 basis). [e] Power plant sizes range from approximately 400-800 MW without capture and 300-700 MW with capture. [f] Capacity factors vary from 65-85% for coal plants and 50-95% for gas plants (average for each=80%). [g] Hydrogen plant feedstocks are natural gas ($4.7-5.3/GJ) or coal ($0.9-1.3/GJ); some plants in dataset produce electricity in addition to hydrogen. [h] Fixed charge factors vary from 11-16% for power plants and 13-20% for hydrogen plants. [i] All costs include CO_2 compression but not additional CO_2 transport and storage costs (see Chapter 8 for full CCS costs).

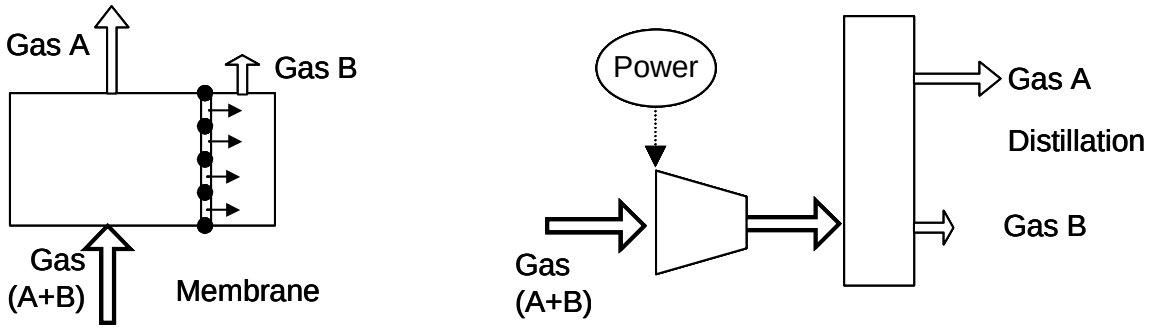
Figures



5 **Figure 3.1.** CO_2 capture systems (adapted from BP).



a) Separation with sorbents/solvents



b) Separation with a membrane *c) Separation by cryogenic distillation*

10

Figure 3.2. General schemes of the main separation processes relevant for CO_2 capture. The gas removed in the separation may be CO_2, H_2 or O_2. In Figures 3.2b and 3.2c one of the separated gas streams (A and B) is a concentrated stream of CO_2, H_2 or O_2 and the other is a gas stream with all the remaining gases in the original gas (A+B).

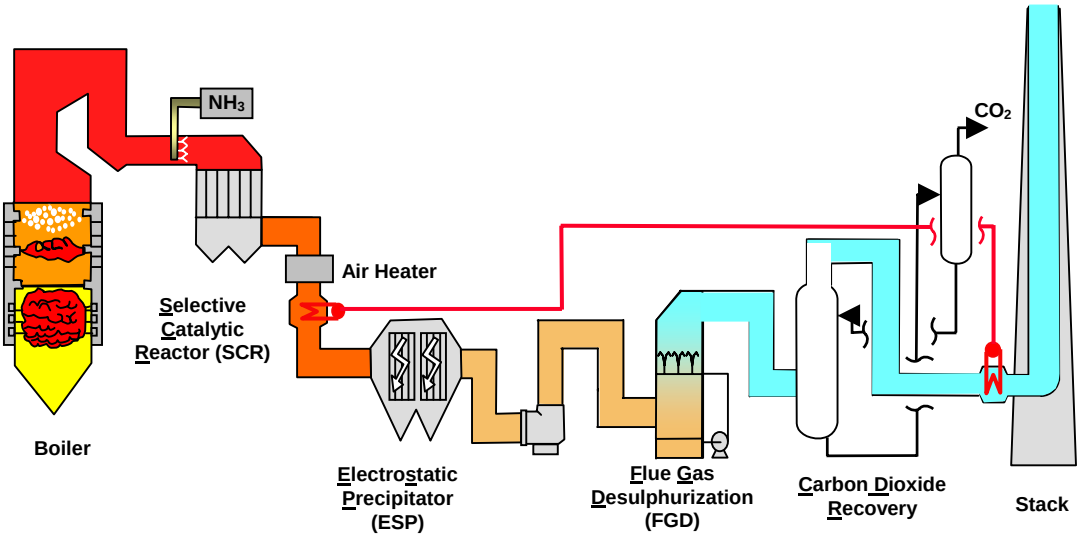


Figure 3.3. Schematic of a pulverised coal-fired power plant with an amine-based CO_2 capture system and other emission controls.

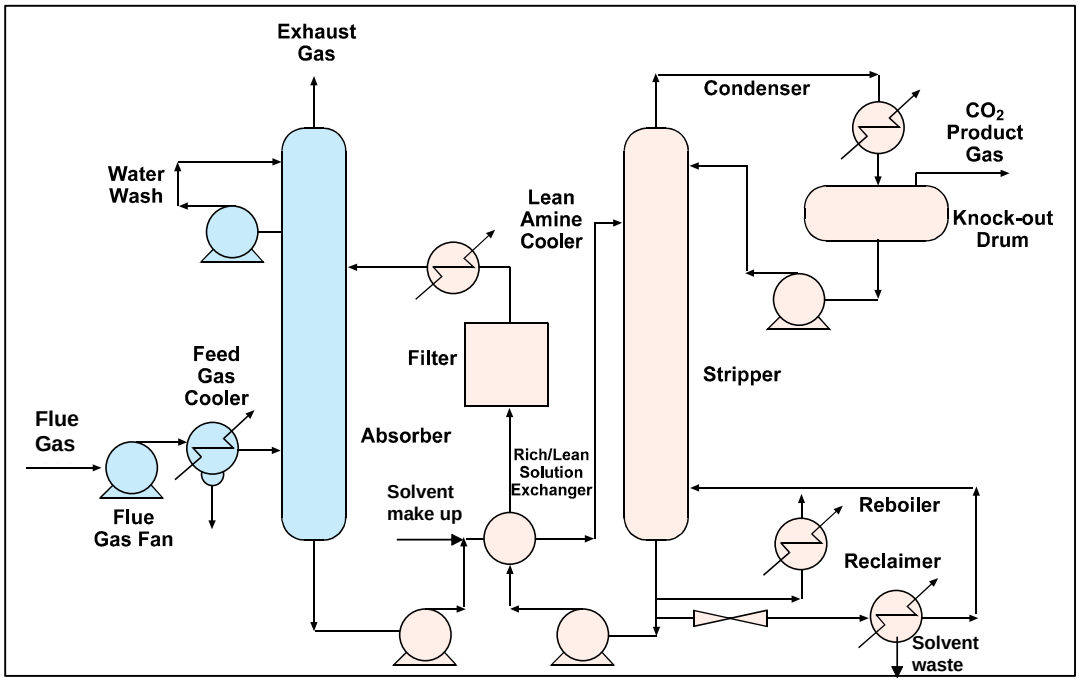


Figure 3.4. Process flow diagram for CO_2 recovery from flue gas by chemical absorption.

Figure 3.5. CO_2 capture plant in Malaysia using a 200 tonnes/day KEPCO/MHI chemical solvent process (Courtesy of Mitsubishi).

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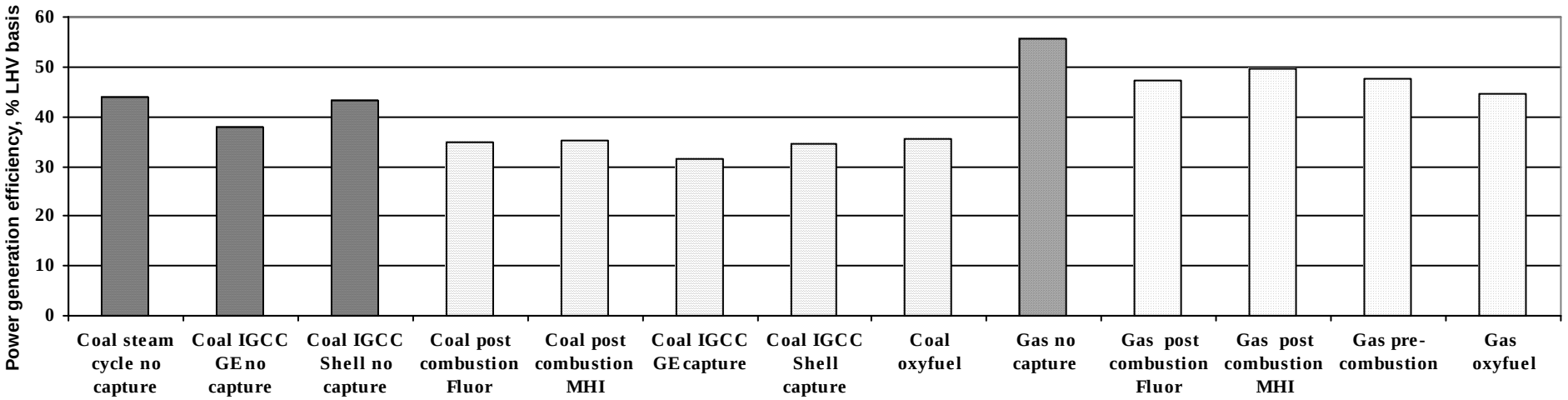

Figure 3.6. Thermal efficiencies of power plants with and without CO_2 capture, % LHV basis (Source data: Davison 2005, IEA GHG 2004, IEA GHG 2003, IEA GHG 2000b, Dillon *et al.*, 2005).

a. The efficiencies are based on a standard set of plant design criteria (IEA GHG 2004).

b. The coal steam cycle plants, including the post-combustion capture and oxy-fuel plants, are based on ultra-supercritical steam (29MPa, 600C superheat, 620C reheat). The IGCC and natural gas pre and post combustion capture plants are based on GE 9FA gas turbine combined cycles. The natural gas oxy-fuel plant is based on a CO_2 recycle gas turbine, as shown in figure 3.10, with different operating pressures and temperatures but similar mechanical design criteria to that of the 9FA.

c. Data are presented for two types of post-combustion capture solvent: MEA (Fluor plant designs) and KS-1 (MHI plant designs). The solvent desorption heat consumptions are 3.2 and 2.7 MJ/kg CO_2 captured respectively for the coal plants and 3.7 and 2.7 MJ/kg for the natural gas plants.

d. Data are presented for IGCC plants based on two types of gasifier: the Shell dry feed/heat recovery boiler type and the GE (formerly Texaco) slurry feed water quench type.

e. The natural gas pre-combustion capture plant is based on partial oxidation using oxygen.

f. The oxy-fuel plants include cryogenic removal of some of the impurities from the CO_2 during compression. Electricity consumption for oxygen production by cryogenic distillation of air is 200 kWh/ tonne O_2 at atmospheric pressure for the coal plant and 320 kWh/ tonne O_2 at 40 bar for the natural gas plant. Oxygen production in the IGCC and natural gas pre-combustion capture plants is partially integrated with the gas turbine compressor, so comparable data cannot be provided for these plants.

g. The percentage CO_2 capture is 85-90% for all plants except the natural gas oxy-fuel plant which has an inherently higher percentage capture of 97%..

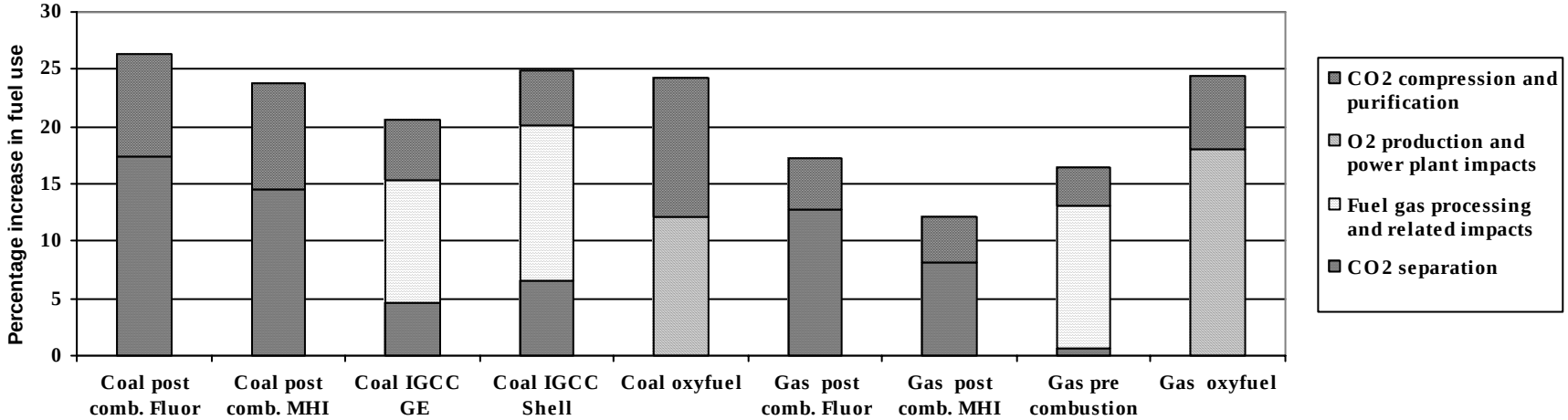

Figure 3.7. Percentage increase in fuel use per kWh of electricity due to CO_2 capture, compared to the same plant without capture (Source data: Davison 2005, IEA GHG 2004, IEA GHG 2003, IEA GHG 2000b, Dillon et. al., 2005).

a. The increase in fuel required to produce a kWh of electricity is calculated by comparing the same type of plant with and without capture. The increase in fuel consumption depends on the type of baseline plant without capture. For example, the increase in energy consumption for a GE IGCC plant with capture compared to a coal steam cycle baseline plant without capture would be 40% as opposed to the lower value shown in the figure that was calculated relative to the same type of baseline plant without capture.

b. The direct energy consumptions for CO_2 separation are lower for pre-combustion capture than for post combustion capture, because CO_2 is removed from a more concentrated, higher pressure gas, so a physical rather than a chemical solvent can be used.

c. The "Fuel gas processing and related impacts" category for IGCC includes shift conversion of the fuel gas and the effects on the gas turbine combined cycle of removal of CO_2 from the fuel gas and use of hydrogen as a fuel instead of syngas. For natural gas pre-combustion capture this category also includes partial oxidation/steam reforming of the natural gas.

d. The energy consumption for CO_2 compression is lower in pre-combustion capture than in post combustion capture because some of the CO_2 leaves the separation unit at elevated pressure.

e. The energy consumption for CO_2 compression in the oxy-fuel processes depends on the composition of the extracted product, namely 75%vol in the coal fired plant and 93%vol in the gas fired plant. Impurities are cryogenically removed from the CO_2 during compression, to give a final CO_2 purity of 96%vol. The energy consumption of the cryogenic CO_2 separation unit is included in the CO_2 compression power consumption.

f. The "Oxygen production and power plant impacts" category for oxy-fuel processes includes the power consumption for oxygen production and the impacts of CO_2 capture on the rest of the power plant, i.e. excluding CO_2 compression and purification. In the coal fired oxy-fuel plant, the efficiency of the rest of the power plant increases slightly, for example due to the absence of a flue gas desulphurisation (FGD) unit). The efficiency of the rest of the gas fired oxy-fuel plant decreases because of the change of working fluid in the power cycle from air to recycled flue gas.

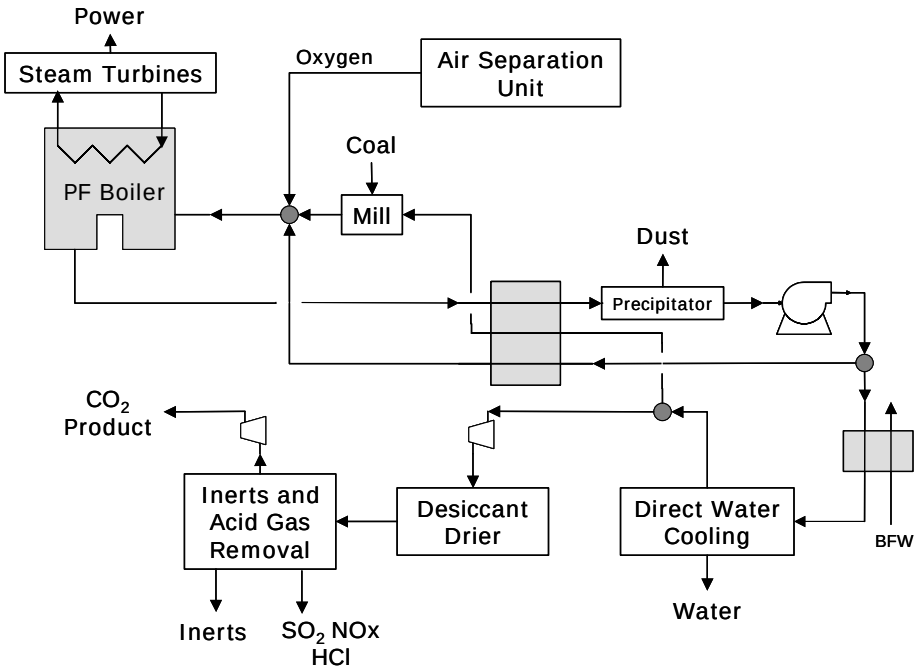

Figure 3.8. Schematic of an Oxy-fuel Pulverised Coal-Fired Power Plant.

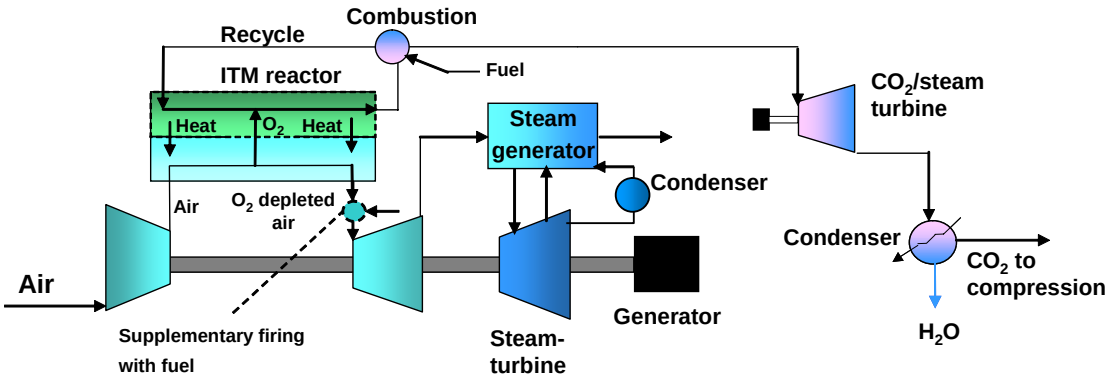

Figure 3.9. Principle flow scheme of the Advanced Zero Emission Power plant cycle.

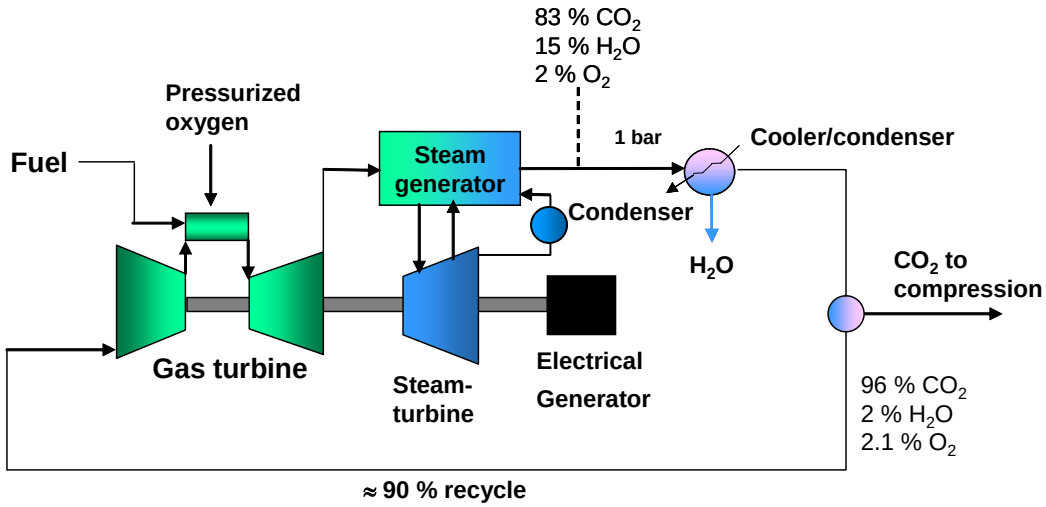

Figure 3.10. Principle of the oxy-fuel gas turbine combined cycle. Exhaust gas is recycled, compressed and used in the combustion chamber to control the temperature entering the turbine.

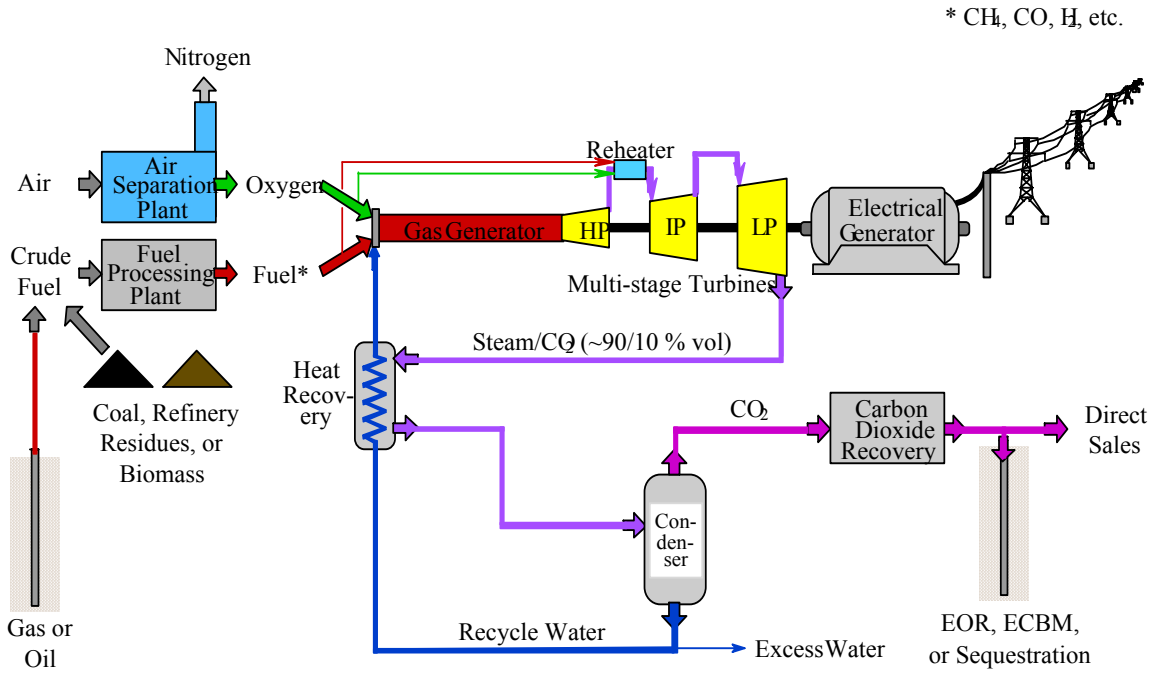

Figure 3.11. Principle of the Clean Energy Systems cycle. The combustion of the fuel and oxygen is cooled by injection of liquid water, which is recycled in the process.

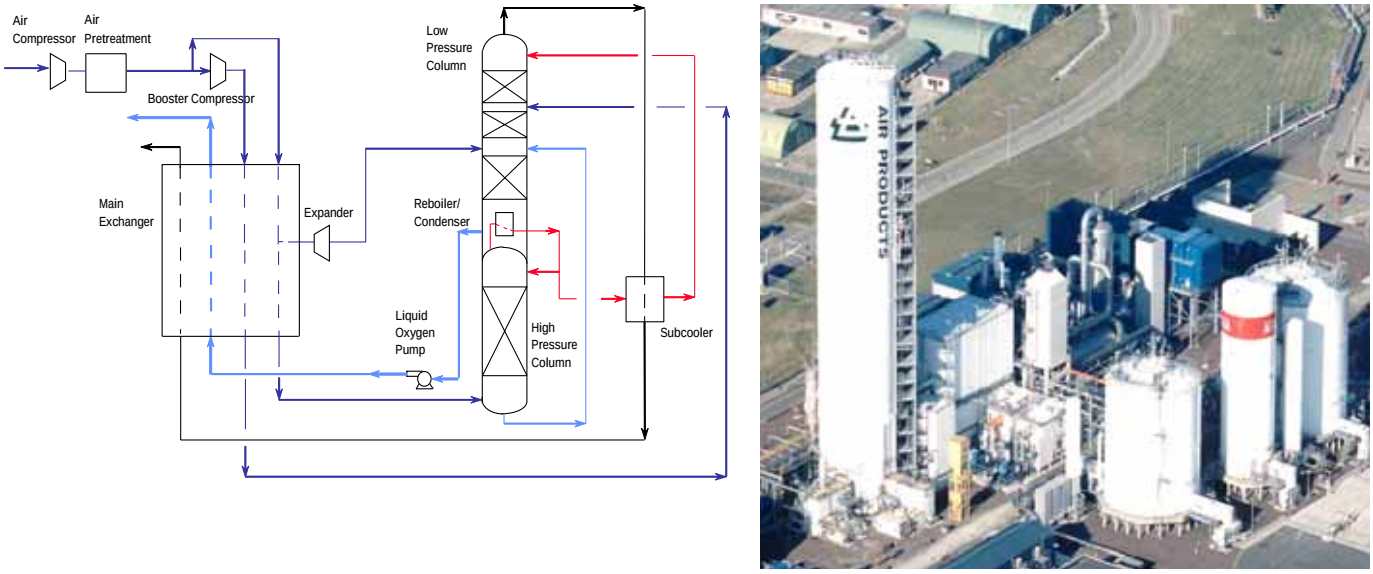

Figure 3.12. Oxygen production by distillation of liquid air. The illustration shows a 3000 tonne/day oxygen plant (courtesy of Air Products).

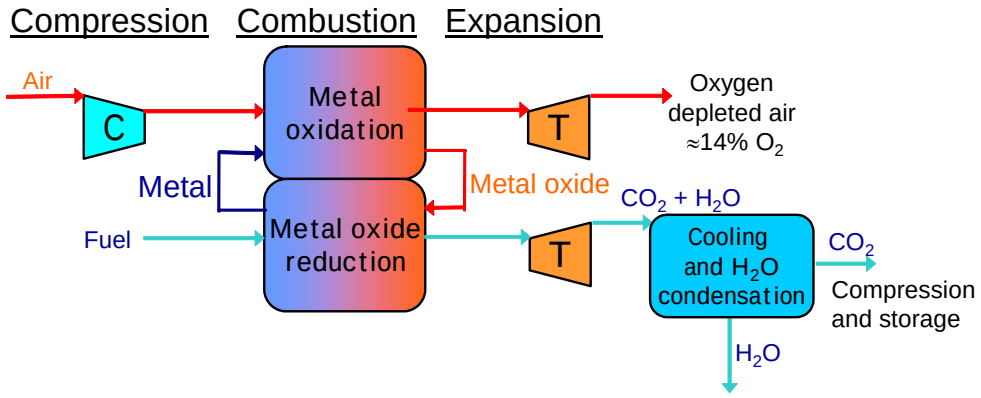

Figure 3.13. The Chemical Looping Combustion principle - in a gas turbine cycle.

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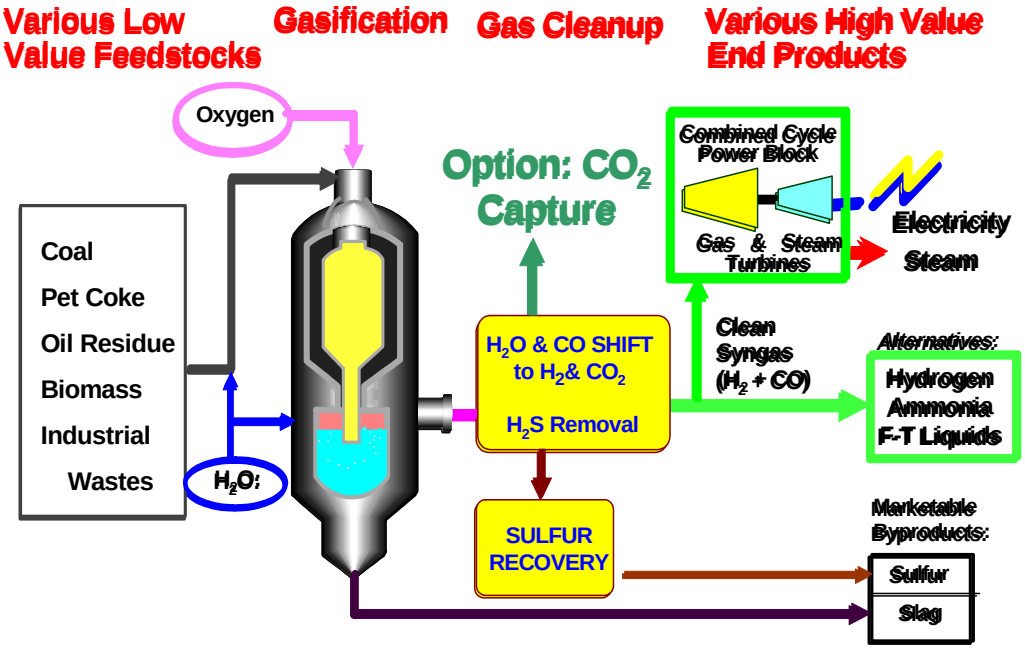

Figure 3.14. Simplified schematic of a gasification process showing options with CO_2 capture and
10 electricity, hydrogen or chemical production.

Figure 3.15. North Dakota coal gasification plant with 3.3 million tonnes/y of CO_2 capture using a cold methanol, physical solvent process (cluster of 4 tall columns in the middle of the picture represent the H_2S and CO_2 capture processes; part of the captured stream is used for EOR with CO_2 storage in Weyburn, Saskatchewan, Canada).

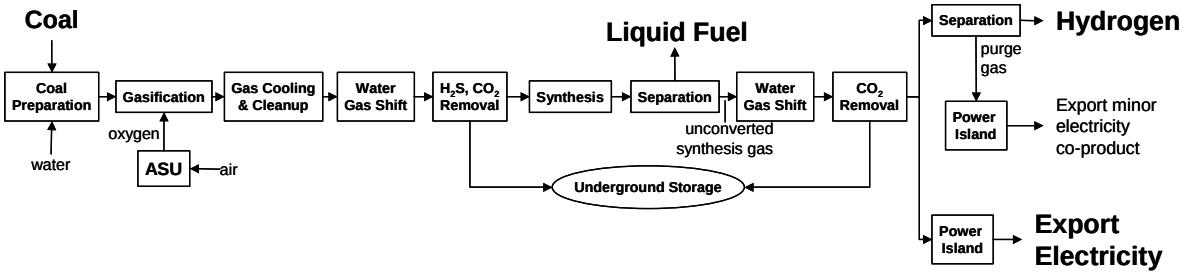

Figure 3.16. Making liquid fuel, electricity, and hydrogen from coal via gasification, with CO_2 capture and storage.

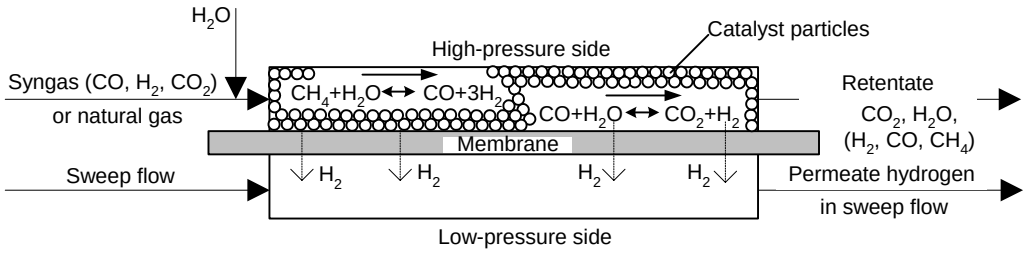

Figure 3.17. Operating principle of a membrane reactor.

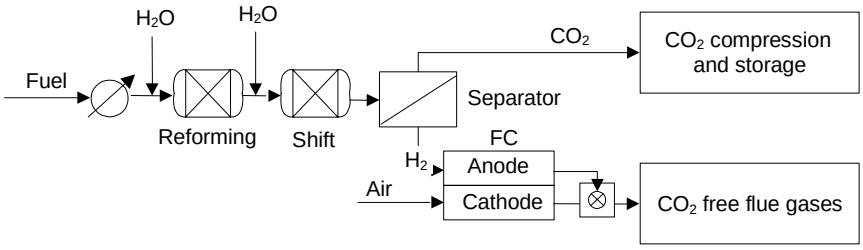

Figure 3.18a. Fuel cell system with pre-fuel cell CO_2 capture. The carbon containing fuel is first completely converted into a mixture of hydrogen and CO_2. Hydrogen and CO_2 are then separated and the H_2 rich fuel is oxidised in the fuel cell to produce electricity. The CO_2 stream is dried and compressed for transport and storage.

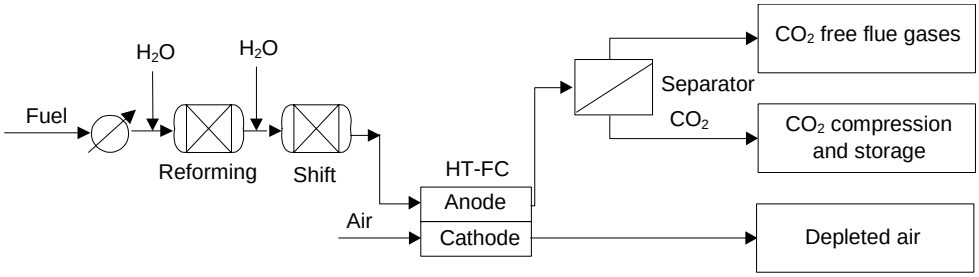

Figure 3.18b. Fuel cell system with post-fuel cell CO_2 capture. The carbon containing fuel is first converted into a syngas. The syngas is oxidised in the fuel cell to produce electricity. At the outlet of the fuel cell CO_2 is separated from the flue gas, dried and compressed for transport and storage.

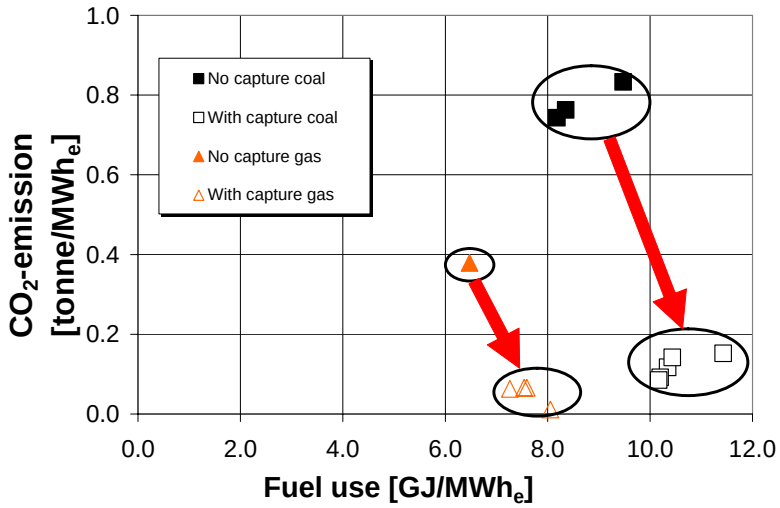

Figure 3.19. Fuel use for a reduction of CO_2 emissions from capture plants (data presented from design studies for power plants with and without capture shown in Figures 3.6 and 3.7).

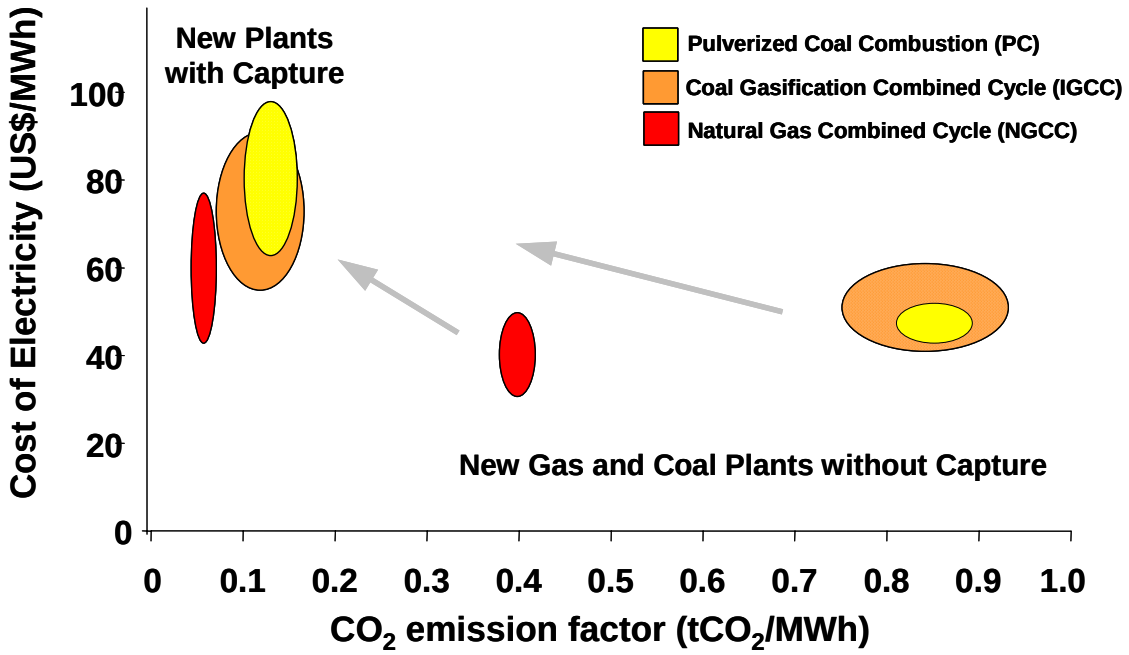

Figure 3.20. Cost of electricity (excluding transport and storage costs) vs. CO_2 emission rate for different reference and capture plants based on current technology. The shaded areas show the Table 3.15 ranges of CO_2 emission rates and levelized cost of electricity (COE) for new PC, IGCC and NGCC plants with and without CO_2 capture. All coal plant data are for bituminous coals only. PC plants are supercritical units only. (See Tables 3.7, 3.9, 3.10 and 3.15 for additional assumptions.) The cost of CO_2 avoided corresponds to the slope of a line connecting a plant with capture and a reference plant without capture (i.e., the change in electricity cost divided by the change in emission rate). Avoidance costs for the same type of plant with and without capture plant are given in Table 3.15. When comparing different plant types, the reference plant represents the least-cost plant that would "normally" be built at a particular location in the absence of a carbon constraint. In many regions today, this would be either a PC plant or an NGCC plant. The cost per tonne of CO_2 avoided can be highly variable, and depends strongly on the costs and emissions of new plants being considered in a particular situation. See Chapter 8 for the full COE and full cost of CO_2 avoided for different plant types.

4 Transport of CO_2

Coordinating Lead Authors
RICHARD DOCTOR (UNITED STATES), ANDREW PALMER (UNITED KINGDOM)

Lead Authors
David Coleman (United States), John Davison (United Kingdom), Chris Hendriks (The Netherlands), Olav Kaarstad (Norway), Masahiko Ozaki (Japan)

Contributing Authors
Michael Austell (United Kingdom)

Review Editors
Ramon Pichs-Madruga (Cuba), Svyatoslav Timashev (Russian Federation)

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Transport is that stage of carbon capture and storage that links sources and storage sites. The beginning and end of "transport" may be defined administratively. "Transport" engages the regulatory framework concerned for public safety that governs pipelines and shipping. In the context of long-distance movement of large quantities of carbon dioxide, pipeline transport is part of current practice. Pipelines routinely carry large volumes of natural gas, oil, condensate and water over distances of thousands of km, both on land and under the sea. Pipelines operate in deserts, over mountains ranges, in heavily-populated areas, in farmland and open range, in the Arctic and sub-Arctic, and in seas and oceans up to 2200 m deep.

Carbon dioxide pipelines are not new: they now extend over more than 2500 km in the western USA, where they carry carbon dioxide from natural sources to enhanced oil recovery projects in the west Texas and elsewhere, and have a capacity of 50 Mt/yr. The carbon dioxide stream ought preferably to be dry and free of hydrogen sulphide, because corrosion is then minimal, and it would be desirable to establish a minimum specification for 'pipeline quality' carbon dioxide. However, it would be possible to design a corrosion-resistant pipeline that would operate safely with a gas that contained water, hydrogen sulphide and other contaminants. Pipeline transport of carbon dioxide through populated areas requires attention to design factors, to overpressure protection and to leak detection, but there is no indication that the problems are any more challenging than those set by hydrocarbon pipelines in similar areas, or that they cannot be resolved.

Liquefied natural gas and petroleum gases such as propane and butane are routinely transported by marine tankers, and that trade is already on a very large scale. Carbon dioxide is transported in the same way, but on a small scale because of limited demand. The properties of liquefied carbon dioxide are not greatly different from those of liquefied petroleum gases, and the technology can be scaled up to large carbon dioxide carriers. A design study has estimated costs for marine transportation of 1 Mt/yr over a distance of 1100 km by one 22000 m^3 marine tanker, and the associated liquefaction, loading and unloading systems.

Liquefied gas can also be carried by rail tankcars and by road tankers, but it is unlikely that they could be attractive options for large-scale carbon dioxide capture and storage projects.

4.1 Introduction

CO_2 is transported in three states, as a gas, liquid, and solid. Commercial-scale transport uses tanks, pipelines and ships for gaseous and liquid carbon dioxide.

Gas transported at close to atmospheric pressure occupies such a large volume that very large facilities are needed. The gas occupies less volume if it is compressed, and compressed gas is transported by pipeline. Volume can be further reduced by liquefaction, solidification or hydration. Liquefaction is an established technology for gas transport by ship as LPG (liquefied petroleum gas) and LNG (liquefied natural gas), and this existing technology and experience can be transferred to liquid CO_2 transport. Solidification needs much more energy compared with other options, and is inferior from a cost and energy viewpoint. Each of the commercially viable technologies is currently used to transport carbon dioxide.

Research and development on a natural gas hydrate chain intended to replace LNG systems is in progress, and the results might be applied to CO_2 ship transport in the future. In pipeline transportation, the volume is reduced by transportation at a high pressure: this is routinely done in gas pipelines, where operating pressures are between 10 and 80 MPa.

A transportation infrastructure that carries carbon dioxide in large enough quantities to make a significant contribution to climate change mitigation will require a large network of pipelines. It may become more difficult to secure pipeline rights-of-way, particularly in highly populated zones that produce large amounts of carbon dioxide. Existing experience has been in zones with low population densities, and safety issues will become more complex in populated areas.

The most economical carbon dioxide capture systems appear to favour CO_2 capture first from pure stream sources such as hydrogen reformers and chemical plants, and next from centralized power and synfuel plants: Chapter 2 discusses this issue in detail. The producers of natural gas speak of "stranded" reserves from which transport to market is uneconomical. A movement towards a decentralized power supply grid may make CO_2 capture and transport much more costly, and it is easy to envision stranded CO_2 at sites where capture is uneconomic.

A regulatory framework for the low-greenhouse gas emissions power industry of the future to make investment decisions will need to emerge. Future power plant owners may find the carbon dioxide transport component one of the leading issues in their decision-making.

4.2 Pipeline systems

4.2.1 Pipeline transportation systems

CO_2 pipeline operators have established minimum specifications for composition. Annex 1 to this chapter gives an example from the Canyon Reef project (section 4.2.2.1). That specification is for gas for an enhanced oil recovery project, and parts of it would not necessarily apply to a CO_2 storage project. A low nitrogen content is important for EOR, but would not be so significant for CCS. A CO_2 pipeline through populated areas might have a lower specified maximum H_2S content.

Dry carbon dioxide does not corrode the carbon-manganese steels generally used for pipelines, as long as the relative humidity (see, for example, Rogers, 1980) is less than 60 per cent; this conclusion continues to apply in the presence of N_2, NO_x and SO_x contaminants. Seiersten (2001) wrote:

> "The corrosion rate of carbon steel in dry supercritical CO_2 is low. For AISI 1080 values around 0.01 mm/yr have been measured at 90-120 bar and 160-180°C during 200 days. Short-term tests confirm this. In a test conducted at 3 and 22°C at 140 bar CO_2, 800 to 1000 ppm H_2S, the corrosion rate for X-60 carbon steel was measured to less than 0.5 μm/yr [0.0005 mm/yr]. Field experience also indicates very few problems with transportation of high-pressure dry CO_2 in carbon steel pipelines. During 12 years, the corrosion rate in an operating pipeline amounts to 0.25-2.5 μm/yr [0.00025 to 0.0025 mm/yr]"

The water solubility limit in high-pressure CO_2 (500 bar) is 5000 ppm at 75°C and 2000 ppm at 30°C. Methane lowers the solubility limit, and H_2S, O_2 and N_2 may have the same effect.

Corrosion rates are much higher if free water is present, and in addition hydrates might form. Seiersten (2001) measured a corrosion rate of 0.7 mm/yr corrosion rate in 150 to 300 hours exposure at 40°C in water equilibrated with CO_2 at 95 bars, and higher rates at lower pressures, and she found little difference between carbon-manganese steel (American Petroleum Institute grade X65) and 0.5 chromium corrosion-resistant alloy. This high corrosion rate makes it unlikely to be practicable to transport wet CO_2 in low-alloy carbon steel pipelines. If the CO_2 cannot be dried, it

may be necessary to build the pipeline of a corrosion-resistant alloy ('stainless steel'): this is an established technology, but the steel cost is much increased.

Box 4.1. *Specimen CO_2 quality specifications [quantities have been metricated]*

"The Product delivered by Seller or Seller's representative to Buyer at the Canyon Reef Carriers Delivery Meter shall meet the following specifications, which herein are collectively called "Quality Specifications":

(a) Carbon Dioxide. Product shall contain at least ninety-five mole percent (95%) of Carbon Dioxide as measured at the SACROC delivery meter.
(b) Water. Product shall contain no free water, and shall not contain more than 4.8×10^{-4} kg/m^3 in the vapor phase.
(c) Hydrogen Sulphide. Product shall not contain more than fifteen hundred (1,500) parts per million, by weight, of hydrogen sulphide.
(d) Total Sulphur. Product shall not contain more than fourteen hundred fifty (1,450) parts per million, by weight, of total sulphur.
(e) Temperature. Product shall not exceed a temperature of 48.9 °C.
(f) Nitrogen. Product shall not contain more than four mole percent (4%) of nitrogen.
(g) Hydrocarbons. Product shall not contain more than five mole percent (5%) of hydrocarbons and the dew point of Product (with respect to such hydrocarbons) shall not exceed -28.9°C.
(h) Oxygen. Product shall not contain more than ten (10) parts per million, by weight, of oxygen.
(i) Glycol. Product shall not contain more than 4×10^{-5} l/m^3 of glycol and at no time shall such glycol be present in a liquid state at the pressure and temperature conditions of the pipeline."

Once the CO_2 has been dried and meets the transportation criteria, the CO_2 is measured and transported to the final use site. All the pipelines have state of the art metering systems that accurately account for sales and deliveries into and out of each line, and SCADA (Supervisory Control and Acquisition of Data) systems for measuring pressure drops, and redundancies built in to allow for emergencies. In the United States, these pipelines are governed by Department of Transportation regulations (See 49CFR195). Movement of CO_2 is best accomplished under high pressure: the choice of operating pressure is discussed in an example below, and the reader is referred to *Appendix I* for a discussion of the physical properties of CO_2.

4.2.2 Existing experience

Table 4.1 lists existing long-distance CO_2 pipelines. Most of the projects listed below are described in greater detail in a report by the UK Department of Trade and Industry (2002). While there are CO_2 pipelines outside the United States, the Permian Basin contains over 90 % of the active CO_2 floods in the world (OGJ, April 15, 2002, EOR Survey). Since that time well over 1,600 km of CO_2 pipelines have been built to service enhanced oil recovery (EOR) in west Texas and nearby states.

Table 4.1. Existing long-distance CO_2 pipelines (Gale, 2002). CO_2 pipelines in North America. Reproduced by courtesy of Oil and Gas Journal.

Figure 4.1. CO_2 pipelines in North America. Reproduced by courtesy of Oil and Gas Journal.

4.2.2.1 Canyon Reef

The first large CO_2 pipeline in the U.S. was the Canyon Reef Carriers, built in 1970 by the SACROC Unit in Scurry County, Texas, USA. Its 352 km moved 12,000 t daily (4.4 Mt/yr) of anthropogenically produced CO_2 from Shell Oil Company gas processing plants in the Texas Val Verde basin. The design issues are discussed below.

4.2.2.2 Bravo Dome Pipeline

Oxy Permian operates this 508 mm (20-inch) line connecting the Bravo Dome CO_2 field with other major pipelines. It is capable of carrying 7.3 Mt/yr.

4.2.2.3 Cortez Pipeline

Built in 1982 to supply CO_2 from the McElmo Dome in S.E. Colorado, the 762 mm (30-inch), 803 km pipeline carries approximately 20 Mt CO_2/yr to the CO_2 hub at Denver City, TX. The line starts near Cortez, CO, and crosses the Rocky Mountains, where it interconnects with other CO_2 lines. In the present context, recall that one 1000 MW coal-fired power station produces about 7 Mt CO_2/yr, and so one Cortez pipeline could handle the emissions of three of those stations.

The Cortez Pipeline passes through two built-up areas, Placitas, NM (30 km north of Albuquerque, NM) and Edgewood/Moriarty, NM (40 km east of Albuquerque). The line is buried at least 1 m deep and is marked within its right of way. Near houses and built up areas it is marked more frequently to ensure the residents are aware of the pipeline locations. The entire pipeline is patrolled by air every two weeks, and in built up areas is frequently patrolled by employees in company vehicles. The public education program includes the mailing of a brochure describing CO_2, signs of a leak and where to report a suspected leak, together with information about the operator and the one-call centre.

4.2.2.4 Sheep Mountain Pipeline

BP operates this 610 mm (24-inch) 772 km line capable of carrying 9.2 Mt CO_2/yr from another naturally occurring source in S.E. Colorado. It connects to the Bravo Dome line and into the other major carriers at Denver City.

4.2.2.5 Weyburn Pipeline

This 330 km 356 and 305 mm diameter system carries more than 5000 t/day (1.8 Mt/yr) of CO_2 from the Great Plains Synfuels Plant near Beulah, ND to the Weyburn EOR project in Saskatchewan. The composition of the gas carried by the pipeline is typically CO_2 96%, H_2S 0.9%, CH_4 0.7%, C2+ hydrocarbons 2.3%, CO 0.1%, N_2 less than 300 ppm, O_2 less than 50 ppm, H_2O less than 20 ppm (UK Department of Trade and Industry, 2002). The delivery pressure at Weyburn is 15.2 MPa. There are no intermediate compressor stations. The amount allocated to build the pipeline was M$ 110 (0.33 M$/km) in 1997.

4.2.3 Design

The physical, environmental and social factors that determine the design of a pipeline are summarised in a design basis, which is then the input to the conceptual design. This includes a system definition for the preliminary route and design aspects for cost estimating and concept definition purposes. It is also necessary to consider the process data defining the physical characteristics of product mixture transported, the optimal sizing and pressures for the pipeline, and

the mechanical design such as the operating, valves, pumps, compressors, seals, etc. The topography of the pipeline right-of-way must be examined. Topography may include mountains, deserts, river and stream crossings, and for offshore pipelines the differing challenges of very deep or shallow water, and uneven seabed. It is also important to include geotechnical considerations. For example, is this pipeline to be constructed on thin soil overlaying granite? The local environmental data needs to be included, the annual variation in temperature during operation and during construction, potentially unstable slopes, frost heave, seismic activity; water depth, sea currents, permafrost, ice gouging in Arctic seas, biological growth, aquifers, other environmental considerations such as protected habitats. The next set of challenges is how the pipeline will accommodate existing and future infrastructure – road, rail, pipeline crossings, military/governmental restrictions as well as the possible impact of other activities – shipping lanes, rural or urban, fishing restrictions, conflicting uses such as dredging. Finally, this integrated study will serve as the basis for a safety review.

Conceptual Design

The conceptual design includes the following components:

- Mechanical design. This follows standard procedures, described in detail in (Palmer et al., 2004).
- Stability design. Standard methods and software are used to perform stability calculations, offshore (Veritec, 1988) or onshore, though the offshore methods have been questioned. New guidelines for stability will be published in 2005 by Det Norske Veritas and will be designated DNV-RP-F109 On-Bottom Stability
- Protection against corrosion. This is a well-understood subject: its application to CO_2 pipelines is described below.
- Trenching and backfilling. Onshore lines are usually buried to depth of 1 m. Offshore lines are almost always buried in shallow water. In deeper water pipelines smaller than 400 mm are trenched and sometimes buried to protect them against damage by fishing gear.
- CO_2 pipelines may be more subject to longitudinal running fracture than hydrocarbon gas pipelines. Fracture arresters are installed at intervals of about 500 m.

West (1974) describes the design of the SACROC CO_2 pipeline (section 4.2.2.1 above). The transportation options examined were:

(i) a low-pressure CO_2 gas pipeline operating at a maximum pressure of 4.8 MPa;
(ii) a high-pressure CO_2 gas pipeline operating at a minimum pressure of 9.6 MPa, so that the gas would remain in a dense phase state at all temperatures;
(iii) a refrigerated liquid CO_2 pipeline;
(iv) road tank trucks;
(v) rail tankers, possibly in combination with road tank trucks.

The tank truck and rail options cost more than twice as much as a pipeline. The refrigerated pipeline was rejected because of cost and technical difficulties with liquefaction. The dense phase (Option-ii) was 20 per cent cheaper than a low-pressure CO_2 gas pipeline (Option-i). The intermediate 4.8 to 9.6 MPa pressure range was avoided so that two-phase flow would not occur. Dense phase transport also showed an advantage in that the high pressure was in every case required for CO_2 injection at the delivery point.

The final design conforms to the ANSI B31.8 code for gas pipelines and to the DOT regulations applicable at the time. The main 290 km section is 406.4 mm (16 inch) outside diameter, 9.53 mm wall, made from grade X65 pipe (specified minimum yield stress 448 MPa). A shorter 60 km section is 323.85 mm (12.75 inch) outside diameter, 8.74 mm wall, grade X65. Tests showed that

dry CO_2 would not corrode the pipeline steel. 304L corrosion-resistant alloy was used for short sections upstream of the glycol dehydrator. The line is buried to a minimum of 0.9 m, and any point on the line is within 16 km of a block valve.

There are six compressor stations, totalling 60 MW, including a station at the SACROC delivery point. The compressor stations are not equally spaced, and the longest distance between two stations is about 160 km. This is consistent with general practice, but some long pipelines have 400 km or more between compressor stations.

Significant nitrogen and oxygen components in CO_2 would shift the boundary of the two-phase region towards higher pressures, and would require a higher operating pressure to avoid two-phase flow.

4.2.4 Construction: land pipelines

Construction planning can begin either before or after rights of way are secured, but a decision to construct will not come before a legal right to construct a pipeline is secured and all governmental regulations met. Onshore and underwater CO_2 pipelines are constructed in the same way as hydrocarbon pipelines, and for both there is an established and well-understood technology. Subsection 4.2.5 describes underwater construction.

The construction phases of a land pipeline are outlined below. Some of the operations can take place concurrently.

Environmental and social factors may influence the season of the year in which construction takes place. The land is cleared and the trench excavated. The longest lead items come first: urban areas, river and road crossings. Pipe is received into the pipe yard and welded into double joints (24 m long); transported to staging areas for placement along pipe route, welded, tested, coated and wrapped, and then lowered into the trench. A hydrostatic test is carried out, and the line is dried. The trench is then backfilled, and the land and the vegetation are restored.

4.2.5 Underwater pipelines

Most underwater pipelines are constructed by the laybarge method, in which 12 or 24 m lengths of pipe are brought to a dynamically positioned or anchored barge, and welded one by one to the end of the pipeline. The barge moves slowly forward, and the pipeline leaves the barge over the stern, and passes first over a support structure (‘stinger’) and then down through the water in a suspended span, until it reaches the seabed. Some lines up to 450 mm diameter are constructed by the reel method, in which the pipeline is welded together onshore, wound onto a reel on a ship, and then unwound from the reel into its final position. Some short lines and lines for shore crossings in shallow water are constructed by various tow and pull methods, in which the line is welded together onshore and then pulled into its final location.

If the design requires that the pipeline be trenched, that is usually done after it has been laid on the seabed, by a jetting sled, a plough or a mechanical cutting device that is pulled along the line. In shore crossings and in very shallow water, on the other hand, the trench is often excavated before the pipeline is laid, and that is done by dredgers, backhoes or draglines in soft sediments, or in rock by blasting followed by clamshell excavators. Many shore crossings are drilled horizontally from the shore, and that eliminates many uncertainties associated with the surf zone, as well as reducing the environmental impact of construction.

Underwater connections are made by various kinds of mechanical connection systems, or by hyperbaric welding (in air under the local hydrostatic pressure) or by lifting the pipe ends above the surface, welding them together and lowering the connected line to the bottom.

These technologies are established and understood (Palmer and King, 2004). Underwater pipelines up to 1422 mm in diameter have been constructed in many different environments, and pipelines have been laid in depths up to 2200 m. Figure 4.2 plots the diameters and maximum depths of major deepwater pipelines constructed up to 2004. The difficulty of construction is roughly proportional to the depth multiplied by the diameter, and the maximum value of that product has multiplied fourfold since 1980. Still larger and deeper pipelines are technically feasible with today's technology.

Figure 4.2. Pipelines in deep water.

4.2.6 Operations

Operational aspects of pipelines divide into three areas: daily operations, maintenance, and health, safety and environment. Operations of a CO_2 pipeline in the USA, for instance, must follow federal operations guidelines (49CFR 195). Overall operational considerations include training, inspections, safety integration, signs and pipeline markers, public education, damage prevention programs, communication, facility security and leak detection. Pipelines outside the USA generally have similar regulatory operational requirements.

Personnel are a central part of operations, and they must be qualified. Personnel are required to be continuously trained and updated on safety procedures, including safety procedures that apply to contractors working on or near to the pipeline, as well as to the public.

Operations includes daily maintenance, and scheduled plan and policy for inspecting, maintaining and repairing all equipment on and supporting the line and the pipeline itself, including valves, compressors, pumps, tanks, rights of way, public signs and line markers as well as periodic pipeline fly-overs.

Long-distance pipelines are instrumented at intervals so that the flow can be monitored. The monitoring points, compressor stations and block valves are tied back to a central operations centre. Computers control much of the operation, and manual intervention is necessary only in unusual upset or emergency conditions. The system has inbuilt redundancies to prevent loss of operational capability if some component fails.

Pipelines are cleaned and inspected by 'pigs', piston-like devices driven along the line by the gas pressure. Pigs have reached a high level of sophistication, and can measure internal corrosion, mechanical deformation, external corrosion, the precise position of the line, and the development of spans in underwater lines. Further functionality will develop as pig technology evolves, and there is no reason why pigs used for hydrocarbon pipelines should not be used for carbon dioxide.

Pipelines are also monitored externally. Land pipelines are inspected from the air, at intervals agreed between the operator and the regulatory authorities. Inspection from the air detects unauthorised excavation or construction before damage occurs. Underwater pipelines are monitored by remotely operated vehicles, small unmanned submersibles that move along the line and make video records, and in the future by autonomous underwater vehicles that do not need to be connected to a mother ship by a cable. Some pipelines have independent leak detection systems that

find leaks acoustically, or by measuring chemical releases, or by picking up pressure changes or small changes in mass balance. This technology is available and routine.

4.3 Ships for CO_2 transportation

4.3.1 Marine transportation system

CO_2 is continuously captured at the plant on land, but the cycle of ship transport is discrete, and so a marine transportation system includes temporary storage on land and a loading facility. The capacity, service speed, number of ships and shipping schedule will be planned considering the capture rate of CO_2, transport distance, social and technical restrictions, etc. This issue is of course not special to the case of CO_2 transport. CO_2 transportation by ship has similarities to liquefied petroleum gas (LPG) transportation by ship.

What happens at the delivery point depends on the CO_2 storage system. If the delivery point is onshore, the CO_2 is unloaded from the ships into temporary storage tanks. If the delivery point is offshore – as in the ocean storage option – ships might unload to a platform, to a floating storage facility (similar to a floating production and storage facility routinely applied to offshore petroleum production), to a single-buoy mooring, or directly to a storage system.

4.3.2 Existing experience

The use of ships for transporting CO_2 across the sea is today in an embryonic stage. World wide there are only four small ships used for this purpose. Those ships transport liquefied food grade CO_2 from large point sources of concentrated carbon dioxide such as ammonia plants in Northern Europe to coastal distribution terminals in the consuming regions. From these distribution terminals CO_2 is transported to the customers either by tanker trucks or in pressurised cylinders. Design work is ongoing in Norway and Japan for larger CO_2 ships and their associated liquefaction and intermediate storage facilities.

4.3.3 Design

For the design of hull and tank structure of liquid gas transport ships, such as LPG carriers and LNG carriers, the International Maritime Organization adopted the International Gas Carrier Code in order to prevent the significant secondary damage from accidental damage to ships. CO_2 tankers are designed and constructed under this code.

There are three types of tank structure for liquid gas transport ships: pressure type, low temperature type and semi-refrigerated type. The pressure type is designed against the boiling pressure of the cargo gas under the air temperature condition. The low temperature type is on the other hand designed for sufficient low temperature to keep cargo gas as a liquid under the atmospheric pressure. Most small gas carriers are pressure type, and large LPG and LNG carriers are low temperature type.

Low temperature type is suitable for mass transport because tank size restriction is not severe. The semi-refrigerated type including the existing CO_2 carriers is designed under the combined conditions of temperature and pressure that is necessary for cargo gas to be kept as liquid. Some tankers as semi-refrigerated LPG carriers are designed to be applicable to the range of cargo conditions between normal temperature/high pressure and low temperature/atmospheric pressure.

Appendix I to this report includes the phase diagram of CO_2. At atmospheric pressure, CO_2 is a gas phase or as solid phase depending on the temperature. Lowering the temperature at atmospheric pressure cannot by itself liquefy CO_2, only make so-called 'dry ice' or solid CO_2. Liquid CO_2 can only exist at a combination of low temperature and pressures well above atmospheric. A CO_2 cargo tank should therefore be the pressure type or the type to keep CO_2 in liquid phase. For the economical mass transport of CO_2, the semi-refrigerated type is preferred by ship designers, and the design point of the cargo tank would be around –54 degree C / 6 bars to –50 degree C / 7 bars, that is near the triple point of CO_2. According to a standard design of semi-refrigerated type of LPG carrier whose cargo design point is –50°C and 700 kPa, the volume is 22,000 m^3. Figure 4.3 below shows a designer's conceptual plan of a CO_2 tanker whose cargo tanks are insulated pressure vessel made of steel suitable for low temperature service.

CO_2 could leak to the atmosphere during transportation. The total loss to the atmosphere from ships is between 3 and 4% per 1000 km, counting both boil-off and exhaust from the ship's engines; both components could be reduced by capture and liquefaction, and recapture onshore would reduce the loss to 1 to 2% per 1000 km.

4.3.4 Construction

CO_2 tankers can be constructed using the same technology used to construct existing liquefied gas carriers. The latest LNG carriers reach more than 200,000m^3 capacity. The same type of yards that today build LPG and LNG ships can carry out the construction of a CO_2-tanker. The actual building time will be from one to two years, depending on among other things the ship size.

4.3.5 Operation

4.3.5.1 Loading

Liquid CO_2 is charged from the temporary storage tank to the cargo tank with pumps adapted for high pressure and low temperature CO_2 service. The cargo tanks are first filled and pressurized with gaseous CO_2 to prevent contamination by humid air and the formation of dry ice.

4.3.5.2 Transport to the site

Heat transfer from the environment through the wall of the cargo tank will boil CO_2 and raise the pressure in the tank. It is not dangerous to discharge the CO_2 boil-off gas together with the exhaust gas from the ship's engines, but doing so does of course release CO_2 to the air. The objective of zero CO_2 emissions during the process of capture and storage can be achieved by using a refrigeration unit to capture and liquefy boil-off and exhaust CO_2.

4.3.5.3 Unloading

Liquid CO_2 is unloaded at the destination site. The volume occupied by liquid CO_2 in the cargo tanks is replaced with dry gaseous CO_2, so that humid air does not contaminate the tanks. That CO_2 could be recycled and reliquefied when the tank is refilled.

4.3.5.4 Return to port in ballast, and drydocking

The CO_2 tanker will return to the port for the next voyage. When the CO_2 tanker is in dock for repair or regular inspection, gas CO_2 in cargo tank should be purged with air for safe working. For the first loading after docking, cargo tanks should be fully dried, purged and filled with gas CO_2.

Ships of similar construction with a combination of cooling and pressure are currently operated for carrying other industrial gases.

4.4 Risk, safety, monitoring

4.4.1 Introduction

There are calculable risks and perceivable risks for any transportation option. We are not considering perceivable risks because this is out the scope of the document. Risks in special cases such as military conflicts and terrorist actions have now been investigated. At least two conferences on pipeline safety and security have taken place, and additional conferences and workshops are planned. However, it is unlikely that these will lead to peer-reviewed journal articles because of the sensitivity of the issue.

Pipelines and marine transportation systems have an established and good safety record. Comparison of CO_2 systems with existing systems for long-distance pipeline transportation of gas and oil, or with marine transportation of oil, where the incidence of failure seems to be perceived by the broad community as acceptable in spite of occasional serious pollution incidents such as the *Exxon Valdes* and *Torrey Canyon* disasters; see van Bernem and Lubbe, 1997.

4.4.2 Land pipelines

Land pipelines are built to defined standards, and are subject to regulatory approval and sometimes to independent design reviews. Their routes are frequently the subject of public inquiries. The process of securing regulatory approval generally includes approval of a safety plan, of detailed monitoring and inspection procedures, and of emergency response plans. In densely populated areas the process of planning licensing and building new pipelines may be difficult and time-consuming. In some places it may be possible to convert existing hydrocarbon pipelines into CO_2 pipelines.

Pipelines in operation are monitored internally by pigs (internal pipeline inspection devices), and externally by corrosion monitoring and leak detection systems and by patrols on foot and by aircraft.

The incidence of failure is relatively small. Guijt (2004) and the European Gas Pipeline Incident Data Group (2002) show that the incidence of failure has markedly decreased. Guijt quotes an incident rate of almost 0.0010 /km year in 1972 falling to below 0.0002 /km year in 2002. Most of the incidents refer to very small pipelines, less than 100 mm diameter, principally applied to gas distributions systems. The failure incidence for 500 mm and larger pipelines is very much lower, below 0.00005 /km year. These figures include all unintentional as releases from pipeline whose design pressure is greater than 1.5 MPa, outside the limits of facilities such as compressor stations. They cover many kinds of incident, not all of them serious, and there is substantial variation between pipelines, reflecting factors such as system age and inspection frequency.

The corresponding incident figures for western European oil pipelines have been published by CONCAWE (2002). In 1997-2001 the incident frequency was 0.0003 /km year. The corresponding figure for US onshore gas pipelines was 0.00011 /km year for the period 1986-2002, defining an incident as an event that released gas and caused death, inpatient hospitalisation or property loss of US$ 50,000: that difference in reporting threshold is thought to account for the difference between European and US statistics (Guijt, 2004).

Lelieveld et al. (2005) examined leakage in 2400 km of the Russian natural gas pipeline system, including compressor stations, valves and machine halls, and concluded that "...overall, the leakage from Russian natural gas transport systems is about 1.4% (with a range of 1.0-2.5%), which is comparable with the amount lost from pipelines in the United States (1.5±0.5%)." Those numbers refer to total leakage, not to leakage per km.

Gale (2002) quotes incident statistics for CO_2 pipelines in the USA. In the period 1990-2002 there were 10 incidents, with property damage totalling US$ 469,000, no injuries, and no fatalities. The incident rate was 0.00032 /km year. However, unlike oil and gas, CO_2 does not form flammable or explosive mixtures with air. Existing CO_2 pipelines are mainly in areas of low population density, which would also tend to result in lower average impacts. The reasons for the incidents at CO_2 pipelines were relief valve failure (4 failures), weld/gasket/valve packing failure (3), corrosion (2) and outside force (1). In contrast, the principle cause of incidents for natural gas pipelines is outside force, such as damage by excavator buckets. Penetration by excavators can lead to loss of pipeline fluid and sometimes to fractures that propagate great distances. Preventative measures such as increasing the depth of cover and use of concrete barriers above a pipeline and warning tape can greatly reduce the risk. For example, increasing cover from 1 m to 2 m reduces the damage frequency by a factor of 10 in rural areas and by 3.5 in suburban areas (Guijt, 2004).

CO_2 leaking from a pipeline is a potential physiological hazard for humans and animals. The consequences of CO_2 incidents can be modelled and assessed on a site specific basis using standard industry methods, taking into account local topography, meteorological conditions, population density and other local conditions. A study by Vendrig (2003) has modelled the risks of CO_2 pipelines and booster stations. A property of CO_2 that needs to be considered when selecting a pipeline route is the fact that CO_2 is denser than air and it can therefore accumulate to potentially dangerous concentrations in low lying areas. Any leak transfers $CO_2$to the atmosphere.

If substantial quantities of impurities, particularly H_2S, are included in the CO_2, this could affect the potential impacts of a pipeline leak or rupture. The exposure threshold at which H_2S is immediately dangerous to life or health, according to the National Institute for Occupational Safety and Health, is 100 ppm, compared to 40,000 ppm for CO_2.

If CO_2 is transported for significant distances in densely populated regions, the number of people potentially exposed to risks of CO_2 transportation facilities may be greater than the number exposed to potential risks of CO_2 capture and storage facilities. Public concerns about CO_2 transportation may be a significant barrier to large-scale use of CCS. At present most electricity generation or other fuel conversion plants are built close to energy consumers or sources of fuel supply. New plants with CO_2 capture could be built close to CO_2 storage sites, to minimise CO_2 transportation. However, this may necessitate greater transportation of fuels or electricity, which have their own environmental impacts, potential risks and public concerns. A gathering system would be needed if CO_2 were brought from distributed sources to a trunk pipeline, and for some storage options a distribution system would also be needed: these systems would need to be planned and executed with the same regard to risk as for the trunk pipeline, as they are for hydrocarbon pipeline systems.

4.4.3 Marine pipelines

Marine pipelines are subject to a similar regulatory regime. The incidence of failure in service is again low. Dragging ships' anchors causes some failures, but that only occurs in shallow water (less than 50 m). Very rarely ships sink onto pipelines, or objects fall onto them. Pipelines 400 mm diameter and larger have been found to be safe against damage caused by fishing gear, but smaller

pipelines are trenched to protect them. Damage to underwater pipelines was examined in detail in a conference (Morris, 1995). Palmer and King (2004) examine case studies of marine pipeline failures, and the technologies of trenching and monitoring. Most failures result from human error. Ecological impacts from a CO_2 pipeline accident have yet to be assessed.

Marine pipelines are monitored internally by inspection devices called "pigs" (as described earlier in section 4.2.5), and externally by regular visual inspection from remotely operated vehicles. Some have independent leak detection systems.

4.4.4 Ships

Ship systems can fail in various ways, by collision, foundering, stranding and fire. Perrow's book on accidents (1984) includes many thought-provoking case studies. Many of the ships that he refers to were old, were badly maintained, and were crewed by inadequately-trained people, but it is wrong to think that marine accidents occur only to poorly regulated 'flag-of-convenience' ships. Gottschalk and Stadler (1990) share Perrow's opinion that many marine accidents can be attributed to systems failures and human factors, whereas accidents due to purely technical factors are relatively uncommon.

Ship casualties are well summarised by Lloyds Maritime Information Service. Over 22.5 years between 1978 and 2000, 41086 incidents of varying degrees of severity were identified, and 2129 of them were classified as 'serious' (See Table 4.2).

Table 4.2. Statistics of serious incidents, depending on the ship type.

Tankers can be seen to have higher standards than ships in general. Stranding is the source of most of the tanker incidents that have led to public concern. It can be controlled by careful navigation along prescribed routes, and by rigorous standards of operation. LNG tankers are potentially dangerous, but are carefully designed and appear to be operated to very high standards. There have been no accidental losses of cargo from LNG ships. The LNG tanker *El Paso Paul Kaiser* ran aground at 17 knots in 1979, and incurred substantial hull damage, but the LNG tanks were not penetrated and no cargo was lost. There is an extensive literature on marine transport of liquefied gas, with a strong emphasis on safety: see, for example, Ffooks (1993).

Carbon dioxide tankers and terminals are clearly much less at risk from fire, but there is an asphyxiation risk if collision should rupture a tank. This risk can be minimised by applying to CO_2 the high standards of construction and operation currently applied to LPG.

An accident to a liquid CO_2 tanker might release liquefied gas onto the surface of the sea. Consideration of such an event is a knowledge gap that requires further study, and it would be anticipated that CO_2 releases would not be associated with the long-term environmental impacts of crude oil spills. CO_2 would behave differently from LNG, because liquid CO_2 in a tanker is less cold than LNG but much denser. Its interactions with the sea would be complex: hydrates and ice might form, and temperature differences would induce strong currents. Some of the gas would dissolve in the sea, but some would be released to the atmosphere. If there were little wind and a temperature inversion, clouds of CO_2 gas might lead to asphyxiation and might stop the ship's engines.

The risk can be minimised by careful planning of routes, and by high standards of training and management.

4.5 Legal issues, codes and standards

Transportation of CO_2 by ships and subsea pipelines and transportation across national boundaries is governed by various international legal conventions. Many jurisdictions/states have environmental impact assessment and strategic environmental assessment legislation that will come into consideration for pipeline building. If a pipeline is constructed across another country's territory (e.g. landlocked states) or if it is laid in certain zones of the sea other countries may have the right to participate in the environmental assessment decision-making process or challenge another State's project.

4.5.1 International conventions

Various international conventions could have implications for storage of CO_2, the most significant being the UN Law of the Sea Convention, the London Convention, the Convention on Environmental Impact Assessment in a Transboundary Context (Espoo Convention) and OSPAR (See Chapter 5). The Espoo convention covers environmental assessment, a procedure that seeks to ensure the acquisition of adequate and early information on likely environmental consequences of development projects or activities, and on measures to mitigate harm. Pipelines are subject to environmental assessment. The most significant aspect of the Convention is that it lays down the general obligation of States to notify and consult each other if a project under consideration is likely to have a significant environmental impact across boundaries. In some cases the acceptability of CO_2 storage under these conventions could depend on the method of transportation to the storage site. Conventions that are primarily concerned with discharge and placement rather than transport are discussed in detail in the chapters on ocean and geological storage.

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal came into force in 1992 (UNEP, 2000). It was conceived partly on the basis that enhanced control of transboundary movement of wastes will act as an incentive for their environmentally sound management and for the reduction of the volume of movement. However, there is no indication that CO_2 will be defined as a hazardous waste under the convention except in relation to the presence of impurities such as heavy metals and some organic compounds that may be entrained during the capture of CO_2. Adoption of schemes where emissions of SO_2 and NO_x would be included with the CO_2 may require such a review. Accordingly, the Basel Convention does not appear to directly impose any restriction on the transportation of CO_2 (IEA GHG, 2003a).

In addition to the provisions of the Basel Convention, any transport of CO_2 would have to comply with international transport regulations. There are numerous specific agreements, some of which are conventions and others are protocols of other conventions that apply depending on the mode of transport. There are also a variety of regional agreements dealing with transport of goods. International transport codes and agreements adhere to the Recommendations on the Transport of Dangerous Goods: Model Regulations published by the United Nations. CO_2 in gaseous and refrigerated liquid forms is classified as a non-flammable, non-toxic gas while solid CO_2 (dry ice) is classified under the heading of miscellaneous dangerous substances and articles. Any transportation of CO_2 adhering to the Recommendations on the Transport of Dangerous Goods: Model Regulations can be expected to meet all relevant agreements and conventions covering transportation by whatever means. Nothing in these recommendations would imply that transportation of CO_2 would be prevented by international transport agreements and conventions (IEA GHG, 2003a).

4.5.2 National codes and standards

The transport of CO_2 by pipeline has been practised for over 25 years. Internationally adopted standards such as ASME B31.4, "Liquid transportation systems for hydrocarbons, liquid petroleum gas, anhydrous ammonia and alcohols" and the widely-applied Norwegian standard (DNV, 2000) specifically mention CO_2. , There is considerable experience in the application and use of these standards. Existing standards and codes vary between different countries but gradual unification of these documents is being progressed by international bodies such as ISO and CEN as part of their function. A full review of relevant standards categorised by issues is presented in IEA GHG, 2003b.

Public concern could highlight the issue of leakage of CO_2 from transportation systems, either by rupture or minor leaks, as discussed in section 4.4. It is possible that standards may be changed in future to address specific public concerns. Odorants are often added to domestic low-pressure gas distribution systems, but not to gas in long-distance pipelines, and they could in principle be added to CO_2 in pipelines. Mercaptans are the most effective odorants, and they are naturally present in the Weyburn pipeline system, but they are not generally suitable for this application because they are degraded by O_2 even at very low concentrations (Katz, 1959). Disulphides, thioethers and ring compounds containing sulphur are alternatives. The value and impact of odorisation could be established by a quantitative risk assessment.

4.6 Costs

4.6.1 Costs of pipeline transport

The costs of pipelines can be categorised in three items

- Construction costs
  - Material/equipment costs (pipe, pipe coating, cathodic protection, telecommunication equipment; possible booster stations)
  - Installation costs (labour)
- Operation and maintenance costs
  - Monitoring costs
  - Maintenance costs
  - (Possible) energy costs
- Other costs (design, project management, regulatory filing fees, insurances costs, right-of-way costs, contingencies allowances)

The pipeline material costs depend on the length of the pipeline, the diameter, the amount of CO_2 to be transported and the quality of the carbon dioxide. Corrosion issues are examined in section 4.2.2. Costs assume that CO_2 is delivered form the capture system at 10 MPa.

Figure 4.3 shows capital investment costs for pipelines. Investments are higher when compressor station(s) are required to compensate for pressure loss along the pipeline in longer pipelines or hilly terrain. Compressor stations may be avoided by increasing the pipeline diameter and reducing the flow velocity. Reported transport velocity varies from 1 to 5 m/s. The actual design will be optimised with regard to pipeline diameter, pressure loss (required compressor stations and power) and pipeline wall thickness.

Costs depend on terrain. Onshore pipeline costs may increase by 50 to 100% or more when the pipeline route is congested and heavily populated. Costs also increase in mountains, in nature reserve areas, in areas with obstacles such as rivers and freeways, and in heavily urbanized areas

because of accessibility for construction and additional required safety measures. Offshore pipelines generally operate at higher pressures and lower temperatures than onshore pipelines, and are often but not always 40 to 70% more expensive.

It is cheaper to collect CO_2 from several sources into a single pipeline than to transport smaller amounts separately. Early and smaller projects will face relatively high transport costs, and therefore be sensitive to transport distance, whereas an evolution towards higher capacities (large and wide-spread application) may result in a decrease of transport costs. Implementation of a 'backbone' transport structure may facilitate access to large remote storage reservoirs, but infrastructure of that kind will require large initial upfront investment decisions. Further study is required to determine the possible advantages of such pipeline system.

Figure 4.4 presents onshore and offshore transport costs versus pipeline diameter based on investment cost information from various sources. Figure 4.5 gives a cost window for specific transport as function of the flow. Steel is a cost component for both pipelines and ships, and steel prices have doubled in the two years to 2005: this may be temporary.

Figure 4.3. Total investment costs pipelines from various information sources for offshore and onshore pipelines. Costs exclude possible booster stations.

Figure 4.4. Transport costs derived from various information sources for offshore and onshore pipelines. Costs exclude possible booster stations. Applied is capital charge rate of 15% and load factor of 100%.

Figure 4.5. Transport costs for onshore and offshore pipelines per 250 km. Indicated are high (broken lines) and low range (continuous lines).

4.6.2 Costs of marine transportation systems

Costs of a marine transport system by ship comprise many cost elements. Besides ships, also investment for loading and unloading facilities, intermediate storage, and liquefaction units are required. Costs are further formed by operation (e.g. labour, ship fuel costs, electricity costs, harbour fees), and maintenance costs. An optimal use of installations and ships in the transport cycle is crucial. Extra facilities, for instance expanded storage need, have to be created to be able to anticipate on possible disruptions in the transport system.

The cost of ship transport systems are not known in detail at the present time since none has been implemented at a scale required for CCS projects, i.e. in the range for several million tones of carbon dioxide handling per year. Designs have been out to tender, and a reasonable amount of knowledge is therefore available. Nevertheless, costs estimates vary widely, because no CO_2 shipping chain of this size has been built and economies of scale will have major impact on the cost estimate results.

A ship designed for carrying CO_2 from harbour to harbour costs according to one source about 30-50% more than a similar size semi-refrigerated LPG ship (Statoil, 2004). However, since the density of liquid CO_2 is about 1100 kg/m^3, CO_2 ships will carry more mass than an equivalent LNG- or LPG-ship, where the cargo density is about 500 kg/m^3.

The estimated cost of ships of 20 to 30 kt capacity is between 50 and 70 M$ (Statoil, 2004). Another source (IEA, 2004) estimate ship construction costs at 34 M$ for 10 kt-sized ship, 60 M$

with a capacity of 30 kt, or 85 M$ with a capacity of 50 kt. A time charter rate of about 25 000 US$/day covering capital charges, manning and maintenance is not unreasonable for a ship in the 20 kt carrying capacity range.

The cost for a liquefaction facility is estimated by Statoil (2004) at 35 to 50 M$ for a capacity of 1 Mt per year. The present largest liquefaction unit is 0.35 Mt/yr. IEA (2004) estimates a considerable lower investment for a liquefaction facility, namely 80 M$ for 6.2 Mt/yr. Investment costs are reduced to 30 M$ when carbon dioxide at 100 bar is delivered to the plant. This pressure level is assumed to be delivered from the capture unit. Cost estimates are influenced by local conditions, e.g. absence of sufficient cooling water may call for more expensive ammonia driven cooling cycle. The difference in numbers also reflects the uncertainty accompanied by scaling up of such facilities

A detailed study (Statoil, 2004) considered a marine transportation system for 5.5 Mt/yr. The base case had 20 kt tankers with a speed of 35 km/hour sailing 7600 km on each trip. 17 tankers were required. The annual cost was estimated at 188 M$ excluding liquefaction and 300 M$ including liquefaction, reducing to 232 M$ if compression is allowed for (to avoid double counting). The corresponding specific transport costs are 34, 55 and 42 US$/t. The study also considered sensitivity to distance: for the case excluding liquefaction, the specific costs were 20 US$/t for 500 km, 22 US$/t for 1500 km, and 28 US$/t for 4500 km.

A study executed for the IEA on a comparable ship transportation system shows lower costs. For a distance of 7600 km using 30 kt ships, the costs are estimated at 35 US$/t. These costs are reduced to 30 US$/t for 50 kt ships. The IEA study also showed a stronger cost dependency on distance than the Statoil (2004) study.

It should be noted that ship transport induces more associated CO_2 transport emissions than pipelines, due to additional energy use for liquefaction and fuel use in ships. IEA (2004) estimated 2.5% of extra CO_2 emissions for a transport distance of 200 km and about 18% for 12,000 km. For pipelines the extra CO_2 emissions for each 1000 km are about 1 to 2%.

Ship transport becomes cost-competitive with pipeline transport over larger distances. Figure 4.6 shows an estimate of the costs for transport of 6 Mt/yr by offshore pipeline and by ship. For this the break-even distance, i.e. the distance for which the costs are equal per transport mode, is about 1000 km. Transport of larger quantities will shift the break-even distance towards larger distances. However, the cross-over point beyond which ship transportation becomes cheaper than pipeline transportation is not simply a matter of distance alone. It involves many other factors, among them loading terminals, pipeline shore crossings, water depth, seabed stability, fuel cost, construction costs, different operating costs in different locations, security, and interaction between land and marine transportation routes.

Figure 4.6. Costs, plotted as transportation cost in US$/t CO_2 against distance, for onshore and offshore pipelines, and ship transport. The costs include intermediate storage facilities, harbour fees, fuel costs and loading/unloading activities. Costs include also additional costs for liquefaction compared to compression. Capital charge factor of 11% for all transport options.

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Tables

Table 4.1. Existing long-distance CO_2 pipelines (Gale, 2002). CO_2 pipelines in North America. Reproduced by courtesy of Oil and Gas Journal.

Pipeline	Location	Operator	CO_2 Capacity (Mt/yr)	Length (km)	Year Finished	Origin of CO_2
Cortez	USA	Kinder Morgan	19.3	808	1984	McElmo Dome
Sheep Mountain	USA	BP Amoco	9.5	660	-	Sheep Mountain
Bravo	USA	BP Amoco	7.3	350	1984	Bravo Dome
Canyon Reef Carriers	USA	Kinder Morgan	5.2	225	1972	Gasification plants
Val Verde	USA	Petrosource	2.5	130	1998	Val Verde Gas Plants
Bati Raman	Turkey	Turkish Petroleum	1.1	90	1983	Dodan Field
Weyburn	USA & Canada	North Dakota Gasification Co.	5	328	2000	Gasification Plant
Total			49.9	2591		

Table 4.2. Statistics of serious incidents, depending on the ship type.

Ship type	Number of ships in year 2000	Serious incidents in period 1978-2000	Frequency (incidents/shipyear)
LPG tankers	982	20	0.00091
LNG tankers	121	1	0.00037
Oil tankers	9678	314	0.00144
Cargo/bulk carriers	21407	1203	0.00250

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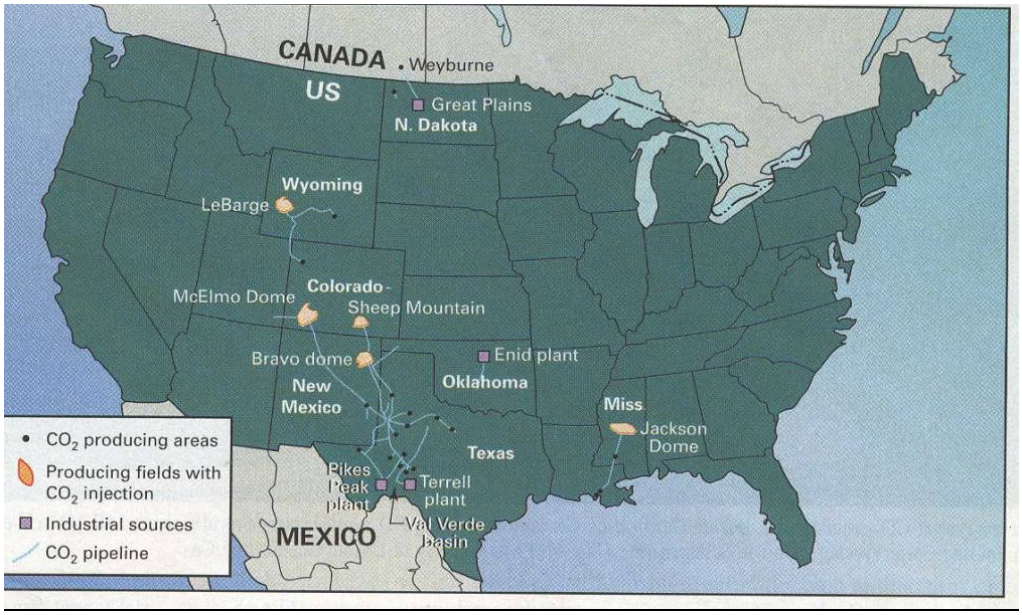


Figure 4.1. CO_2 pipelines in North America. Reproduced by courtesy of Oil and Gas Journal.

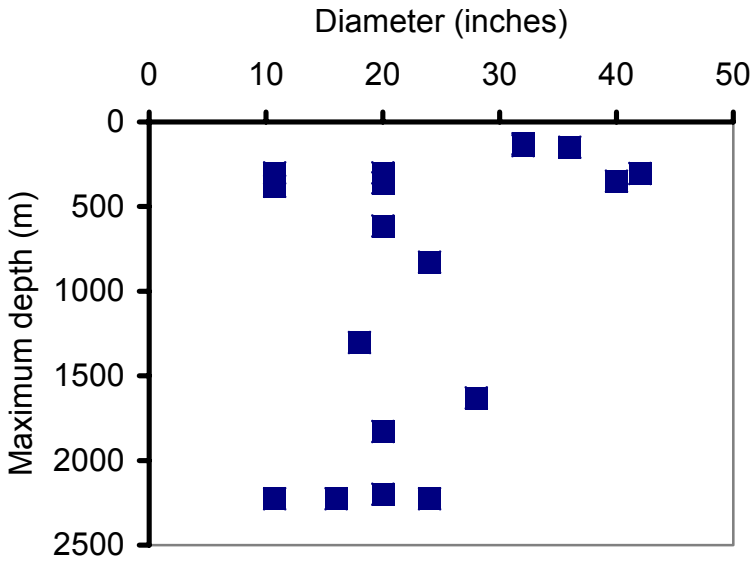


Figure 4.2. Pipelines in deep water.

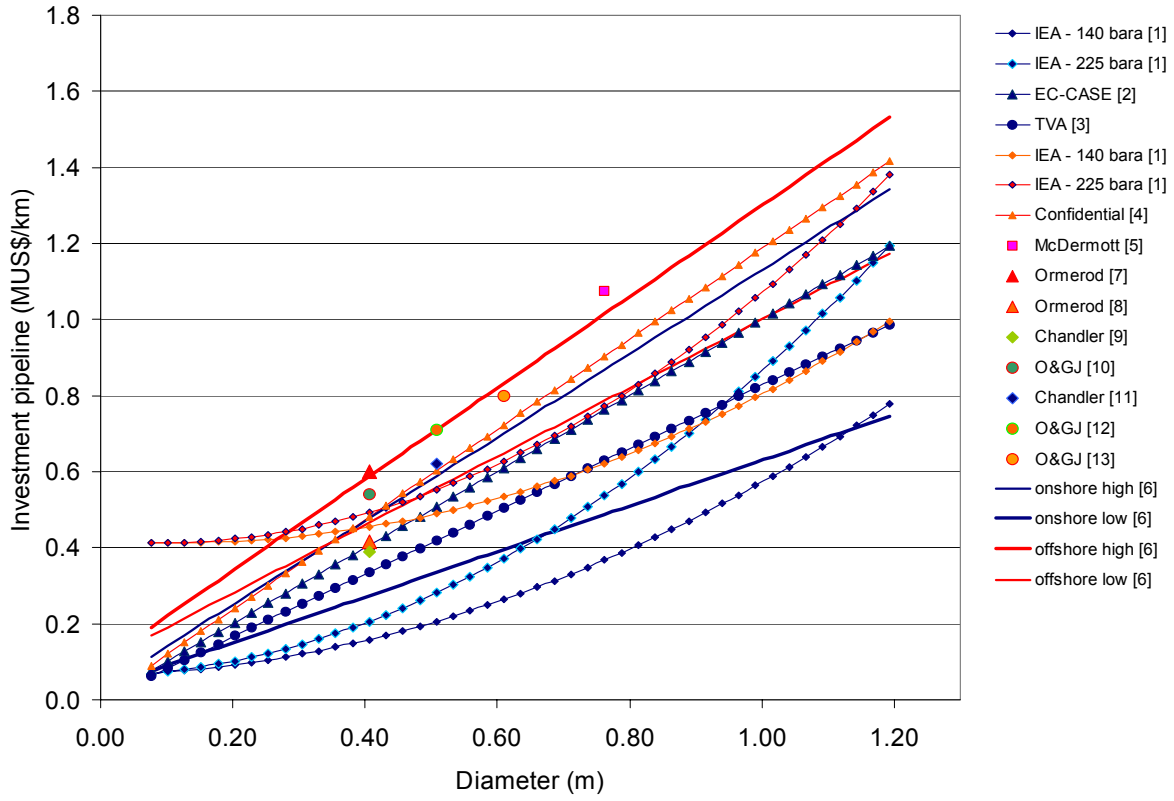
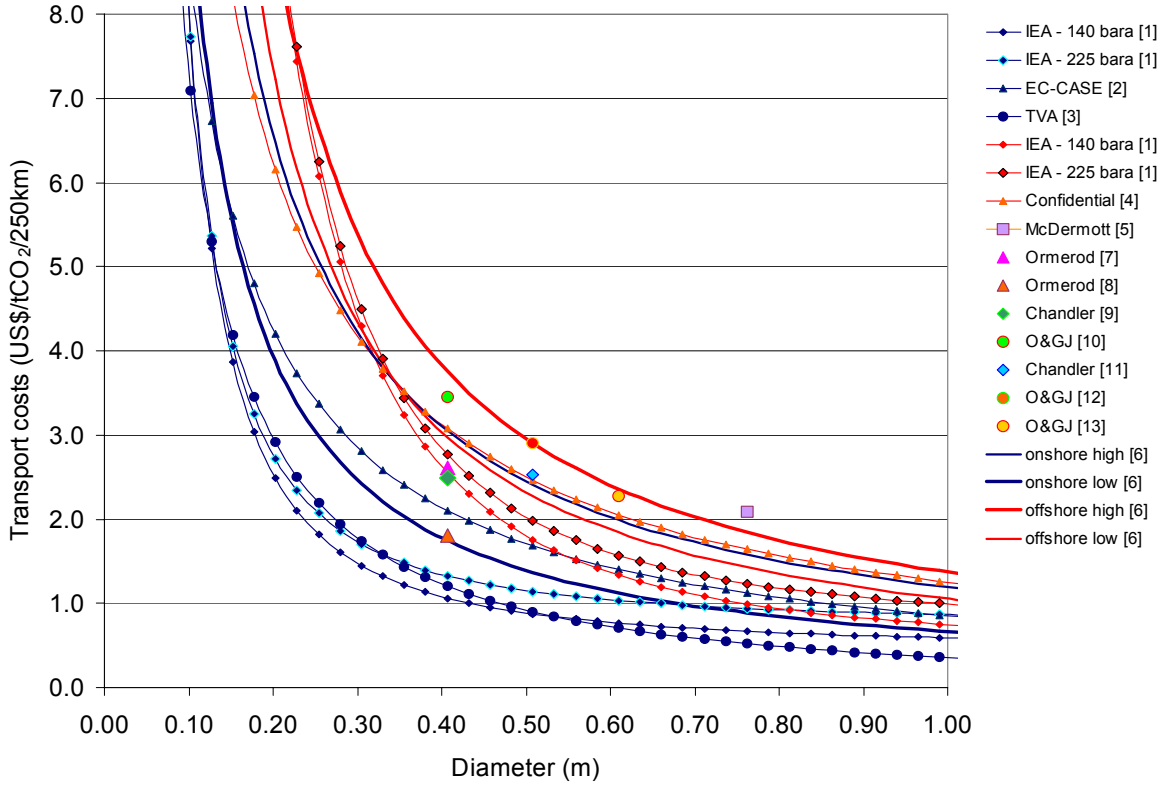


Figure 4.3. Total investment costs pipelines from various information sources for offshore and onshore pipelines. Costs exclude possible booster stations.



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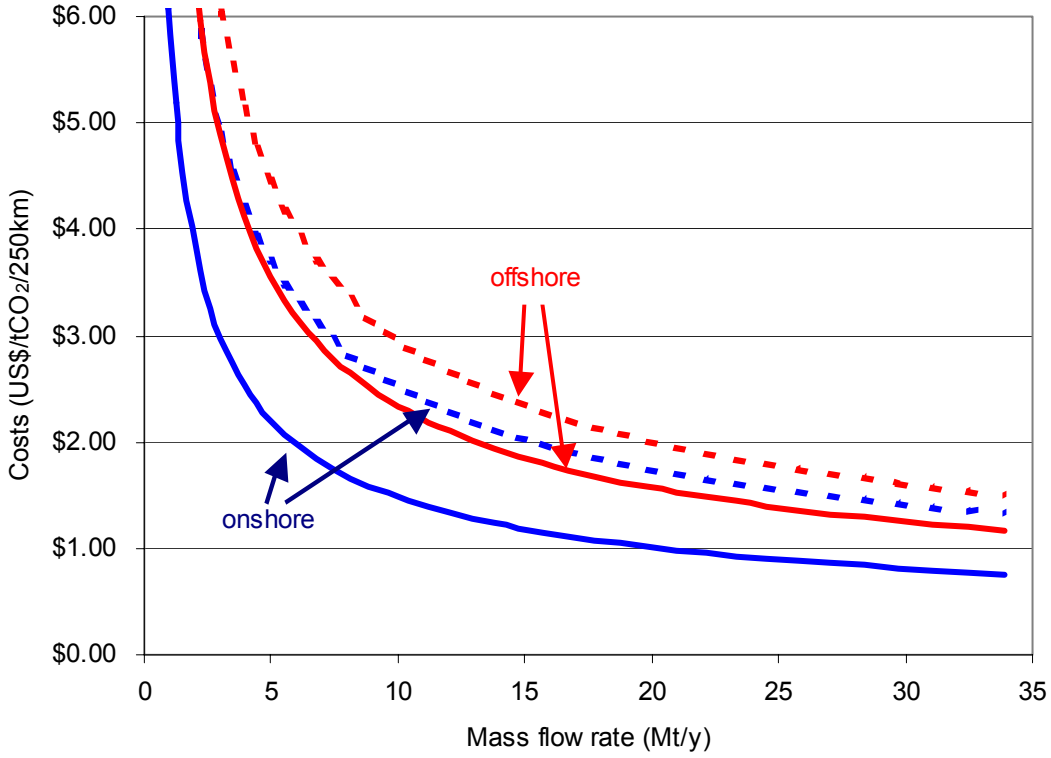

Figure 4.5. Transport costs for onshore and offshore pipelines per 250 km. Indicated are high (broken lines) and low range (continuous lines).

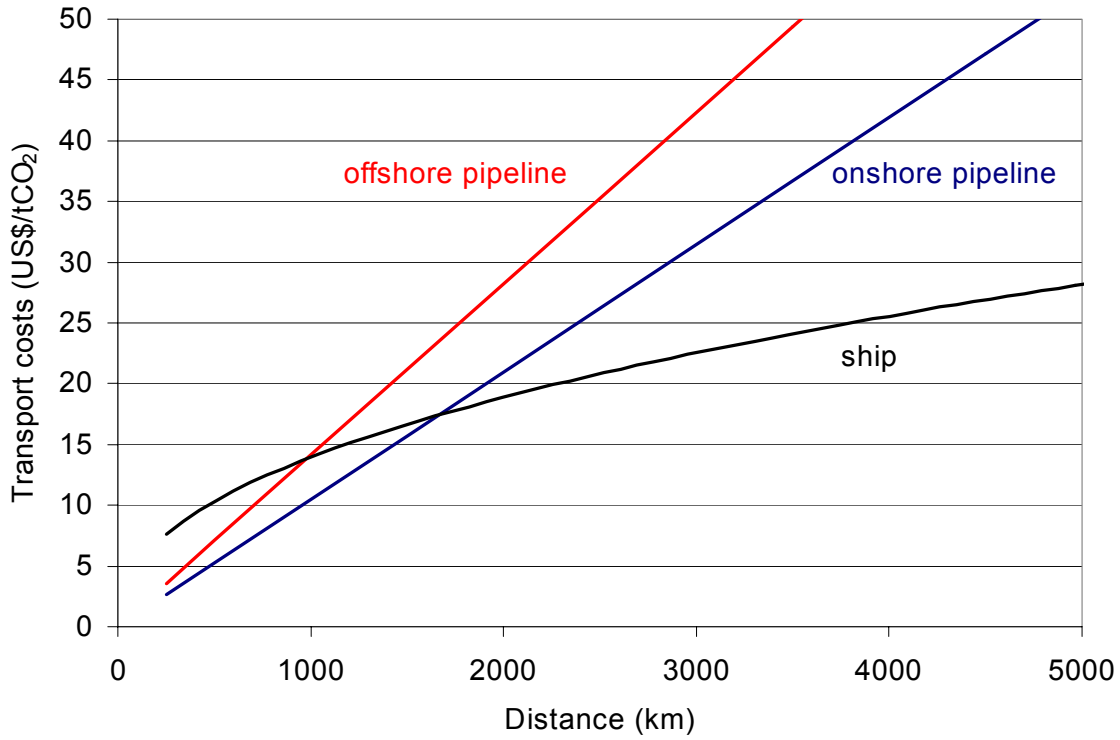

Figure 4.6. Costs, plotted as transportation cost in US$/t CO_2 against distance, for onshore and offshore pipelines, and for ship transport. The costs include intermediate storage facilities, harbour fees, fuel costs and loading/unloading activities. Costs include also additional costs for liquefaction compared to compression. Capital charge factor of 11% for all transport options.

5 Underground geological storage

Coordinating Lead Authors

SALLY BENSON (UNITED STATES), PETER COOK (AUSTRALIA)

Lead Authors

Jason Anderson (United States), Stefan Bachu (Canada), Hassan Bashir Nimir (Sudan), Biswajit Basu (India), John Bradshaw (Australia), Gota Deguchi (Japan), John Gale (United Kingdom), Gabriela von Goerne (Germany), Wolfgang Heidug (Germany), Sam Holloway (United Kingdom), Rami Kamal (Saudi Arabia), David Keith (Canada), Philip Lloyd (South Africa), Paulo Rocha (Brazil), Bill Senior (United Kingdom), Jolyon Thomson (United Kingdom), Tore Torp (Norway), Ton Wildenborg (Netherlands), Malcolm Wilson (Canada), Francesco Zarlenga (Italy), Di Zhou (China)

Contributing Authors

Michael Celia (United States), Bill Gunter (Canada), Jonathan Ennis King (Australia), Erik Lindeberg (Norway), Salvatore Lombardi (Italy), Curt Oldenburg (United States), Karsten Pruess (United States), Andy Rigg (Australia), Scott Stevens (United States), Elizabeth Wilson (United States), Steve Whittaker (Canada)

Review Editors

Günther Borm (Germany), David Hawkins (United States), Arthur Lee (United States)

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Executive summary

Underground accumulation of carbon dioxide (CO_2) is a widespread geological phenomenon, with natural trapping of CO_2 in underground reservoirs. Information and experience gained from the injection and/or storage of CO_2 from a large number of existing EOR and acid gas projects, as well as from the Sleipner, Weyburn, and In Salah projects, indicate that it is feasible to store CO_2 in geological formations as a CO_2 mitigation option. Industrial analogues, including underground natural gas storage projects around the world and acid gas injection projects, provide additional indications that CO_2 can be safely injected and stored at well-characterized and properly managed sites. While there are differences between natural accumulations and engineered storage, injecting CO_2 into deep geological formations at carefully selected sites can store it underground for long periods of time: it is considered likely that 99% or more of the injected CO2 will be retained for 1000 years. Depleted oil and gas reservoirs, possibly coal formations and particularly saline formations (deep underground porous reservoir rocks saturated with brackish water or brine), can be used for storage of CO_2. At depths below ~800 to 1,000 m, supercritical CO_2 has a liquid-like density that provides the potential for efficient utilization of underground storage space in the pores of sedimentary rocks. Carbon dioxide can remain trapped underground by virtue of a number of mechanisms, such as trapping below an impermeable, confining layer (caprock); retention as an immobile phase trapped in the pore spaces of the storage formation; dissolution in the *in situ* formation fluids; and/or adsorption onto organic matter in coal and shale. Additionally, it may be trapped by reacting with the minerals in the storage formation and caprock to produce carbonate minerals. Models are available to predict what happens when CO_2 is injected underground. Also, by avoiding deteriorated wells, or open fractures or faults, injected CO_2 will be retained for very long periods of time. Moreover, CO_2 becomes less mobile over time as a result of multiple trapping mechanisms, further lowering the prospect of leakage.

Injection of CO_2 in deep geological formations uses technologies that have been developed for, and applied by, the oil and gas industry. Well-drilling technology, injection technology, computer simulation of storage reservoir dynamics, and monitoring methods can potentially be adapted from existing applications to meet the needs of geological storage. Beyond conventional oil and gas technology, other successful underground injection practices - including natural gas storage, acid gas disposal and deep injection of liquid wastes - as well as the industry's extensive experience with subsurface disposal of oil-field brines can provide useful information in designing programs for long-term storage of CO_2. Geological storage of carbon dioxide is in practice today beneath the North Sea, where nearly 1 $MtCO_2$ have been successfully injected annually at Sleipner since 1996 and in Algeria at the In-Salah gas field. Carbon dioxide is also injected underground to recover oil. About 30 Mt of nonanthropogenic CO_2 are injected annually, mostly in west Texas, to recover oil from over 50 individual projects, some of which started in the early 1970s. The Weyburn Project in Canada, where currently almost 2 are injected annually, combines enhanced oil recovery (EOR) with a comprehensive monitoring and modeling program to evaluate CO_2 storage. Several more storage projects are under development at this time.

In areas with suitable hydrocarbon accumulations, CO_2-Enhanced Oil Recovery (EOR) may be implemented because of the added economic benefit of incremental oil production, which may offset some of the costs of CO_2 capture, transportation and injection. Storage of CO_2 in coal beds, in conjunction with enhanced coal bed methane (ECBM) production, is potentially attractive because of the prospect of enhanced production of methane, the cleanest of the fossil fuels. This technology, however, is not well developed, and a better understanding of injection and storage processes in coals is needed. Carbon dioxide storage in depleted and oil gas reservoirs is very promising in some areas, because these structures are well known and significant infrastructures are already in place.

Nevertheless, relatively few hydrocarbon reservoirs are currently depleted or near depletion, and CO_2 storage will have to be staged to fit the time of reservoir availability. Deep saline formations are believed to have by far the largest capacity for CO_2 storage and are much more widespread than other options.

While there are uncertainties, the global capacity to store CO_2 deep underground is large. Depleted oil and gas reservoirs are estimated to have a storage capacity from 675 to 900 $GtCO_2$. Deep saline formations are very likely to have a storage capacity of 1,000 $GtCO_2$, and some studies suggest it may be an order of magnitude greater than this, but quantification of the upper range is difficult until additional studies are undertaken. Capacity of unminable coal formations is uncertain, with estimates ranging from as little as 3 $GtCO_2$ up to 200 $GtCO_2$. Potential storage sites are likely to be broadly distributed in many of the world's sedimentary basins, located in the same region as many of the world's emission sources and are likely to be adequate to store a significant proportion of those emissions well into the future.

The cost of geological storage of CO_2 is highly site specific, depending on factors such as the depth of the storage formation, the number of wells needed for injection, and whether the project is onshore or offshore - but costs for storage, including monitoring, appear to lie in the range of U.S. $0.6 to $8.3 per tonne of CO_2 stored. This cost is small compared to present-day costs of CO_2 capture from flue gases, as indicated in Chapter 3. EOR could lead to negative storage costs of US$ 10-16 per tonne of CO_2 for oil prices of US$ 15-20 per barrel, and more for higher oil prices.

Potential risks to humans and ecosystems from geological storage may arise from leaking injection wells, abandoned wells, leakage across faults, and ineffective confining layers. Leakage of CO_2 could potentially degrade groundwater quality, damage some hydrocarbon or mineral resources and have lethal effects on on plants and sub-soil animals. Release of CO_2 back into the atmosphere could also create local health and safety concerns. Avoiding or mitigating these impacts will require careful site selection, effective regulatory oversight, an appropriate monitoring program that provides early warning that the storage site is not functioning as anticipated, and implementation of remediation methods to stop or control CO_2 releases. Methods to accomplish these are being developed and tested.

There are few, if any, national regulations specifically dealing with CO_2 storage, but regulations dealing with oil and gas, groundwater, and the underground injection of fluids can in many cases be readily adapted and/or adopted. However, there are no regulations relating specifically to long-term responsibility for storage. A number of international laws that predate any consideration of CO_2 storage are relevant to offshore geological storage; consideration of whether these laws do or do not permit offshore geological storage is under way.

There are gaps in our knowledge, such as regional storage-capacity estimates for many parts of the world. Similarly, better estimation of leakage rates, improved cost data, better intervention and remediation options, more pilot and demonstration projects, and clarity on the issue of long-term stewardship all require consideration. Despite the fact that more work is needed to improve technologies and decrease uncertainty, there appear to be no insurmountable technical barriers to an increased uptake of geological storage as an effective mitigation option.

5.1 Introduction

5.1.1 What is geological storage?

Carbon dioxide capture and geological storage provide a way to avoid emitting CO_2 to the atmosphere, by capturing CO_2 from major stationary sources (Chapter 3), transporting it usually by pipeline (Chapter 4), and injecting it into suitable deep rock formations. This chapter explores the nature of geological storage and considers its potential as a mitigation option.

The subsurface is the earth's largest carbon reservoir, where the vast majority of the world's carbon is held in coals, oil, gas, organic-rich shales, and carbonate rocks. Geological storage of CO_2 has been a natural process in the earth's upper crust for hundreds of millions of years. Carbon dioxide derived from biological activity, igneous activity, and chemical reactions between rocks and fluids accumulates in the natural subsurface environment as carbonate minerals, in solution, or in a gaseous or supercritical form, either as a gas mixture or as pure CO_2. The engineered injection of CO_2 into subsurface geological formations was first undertaken in Texas, U.S.A., in the early 1970s, as part of enhanced oil recovery (EOR) projects, and has been ongoing there and at many other locations ever since.

Geological storage of anthropogenic CO_2 as a greenhouse gas mitigation option was first proposed in the 1970s, but little research was done until the early 1990s, when the idea gained credibility through the work of individuals and research groups (Marchetti, 1977; Baes et al., 1980; Kaarstad, 1992; Koide et al., 1992; van der Meer, 1992; Holloway and Savage, 1993; Gunter et al., 1993; Bachu et al., 1994; Korbol and Kaddour, 1994). The subsurface disposal of acid gas (a by-product of petroleum production with a CO_2 content of up to 98%) in the Alberta Basin of Canada and in the United States provides additional useful experience. In 1996, the world's first large-scale storage project was initiated by Statoil and its partners at the Sleipner Gas Field in the North Sea.

By the late 1990s, a number of publicly and privately funded research programs were under way in the United States, Canada, Japan, Europe, and Australia. Throughout this time, though less publicly, a number of oil companies became increasingly interested in geological storage as a mitigation option, particularly for gas fields with a high natural CO_2 content such as Natuna in Indonesia, In Salah in Algeria, and Gorgon in Australia. More recently, coal mining companies and electricity-generation companies have started to investigate geological storage as a mitigation option of relevance to their industry.

In a little over a decade, geological storage of CO_2 has grown from a concept of limited interest to one that is quite widely regarded as a potentially important mitigation option (Figure 5.1). There are several reasons for this. First, as research has progressed, and as demonstration and commercial projects have been successfully undertaken, the level of confidence in the technology has increased. Second, there is consensus that a broad portfolio of mitigation options is needed. Third, geological storage (in conjunction with CO_2 capture) could help to make deep cuts to atmospheric CO_2 emissions. However, if that potential is to be realized, the technique must be safe, environmentally sustainable, cost-effective, and capable of being broadly applied. This chapter explores these issues.

Figure 5.1. Location of sites where activities relevant to CO_2 storage are planned or under way.

To geologically store CO_2, it must first be compressed, usually to a dense fluid state known as "supercritical" (Appendix 1). Depending on the rate of increase of temperature with depth

(geothermal gradient), the CO_2 will increase in density, until at depths of about 800 m or greater, the injected CO_2 will be in a dense supercritical state (Figure 5.2).

Figure 5.2. Variation of CO_2 density with depth (Angus et al., 1973), assuming hydrostatic pressure and a geothermal gradient of 25°C/km from 15°C at the surface. Carbon dioxide density increases rapidly at approximately 800 m depth, as the CO_2 reaches a supercritical state. Cubes are representative of the relative volume occupied by the CO_2, and down to 800 m, this volume can be seen to dramatically decrease with depth. At depths below1.5 km, the density and specific volume become nearly constant.

Geological storage of CO_2 can be undertaken in a variety of geological settings in sedimentary basins. Within these basins, oil fields, depleted gas fields, deep coal seams, and saline formations are all possible storage formations (Figure 5.3).

Subsurface geological storage is possible both onshore and offshore, with offshore sites accessed through pipelines from the shore or from offshore platforms. The continental shelf and some adjacent deep-marine sedimentary basins are potential offshore storage sites, but the majority of sediments of the abyssal deep ocean floor are too thin and impermeable to be suitable for geological storage (Cook and Carleton, 2000). In addition to storage in sedimentary formations, some consideration has been given to storage in caverns, basalt, and organic-rich shales (Section 5.3).

Figure 5.3. Options for storing CO_2 in deep underground geological formations (after Cook, 1999).

Fluids have been injected on a massive scale into the deep subsurface for many years, to dispose of unwanted chemicals, pollutants, or by-products of petroleum production, enhance the production of oil and gas, or recharge depleted formations (Wilson et al., 2003). The principles involved in such activities are well established, and in most countries there are regulations governing these activities. Natural gas has also been injected and stored in the subsurface on a large scale in many parts of the world for many years. Injection of CO_2 to date has been done at relatively smallscale, but if it were to be employed to significantly decrease emissions from existing stationary sources, then the injection rates would be at a scale similar to other injection operations under way at present.

But what is the world's geological storage capacity, and does it occur where we need it? These questions were first raised in Chapter 2, but Section 5.3 of this chapter considers geographical matching of CO_2 sources to geological storage sites in detail. Not all sedimentary basins are suitable for CO_2 storage; some are too shallow and others are dominated by rocks with low permeability or poor confining characteristics. Basins suitable for CO_2 storage have characteristics such as thick accumulations of sediments, permeable rock formations saturated with saline water (saline formations), extensive covers of low porosity rocks (acting as seals), and structural simplicity. While many basins show such features, many others do not.

Is there likely to be sufficient storage capacity to meet the world's needs in the years ahead? To consider this issue, it is useful to draw parallels with the terms "resources" and "reserves" used for mineral deposits (McKelvey, 1972). Deposits of minerals or fossil fuels are often cited with very large resource figures, but the "proven" reserve is only some fraction of the resource. The resource is based on the selling price of the commodity, the cost of exploiting the commodity, the availability of appropriate technologies, proof that the commodity exists, and whether the environmental or social impact of exploiting the commodity is acceptable to the community. Similarly, to turn technical geological storage capacity into economical storage capacity, the storage project must be

economically viable, technically feasible, safe, environmentally and socially sustainable, and acceptable to the community. Given these constraints, it is inevitable that the storage capacity that will actually be used will be significantly less than the technical potential. Section 5.3 explores this issue. It is likely that usable storage capacity will exist in many areas where people live and where CO_2 is generated from large stationary sources. This geographical congruence of storage-need and storage-capacity should not come as a surprise, because much of the world's population is concentrated in regions underlain by sedimentary basins (Gunter et al., 2004).

It is also important to know how securely and for how long stored CO_2 will be retained - decades, centuries, millennia or for geological time? To assure public safety, storage sites must be designed and operated to minimize the possibility of leakage. Consequently, potential leakage pathways must be identified, and procedures must be established, to set appropriate design and operational standards as well as monitoring, measurement, and verification requirements. Sections 5.4, 5.6, and 5.7 consider these issues.

In this chapter, we primarily consider storage of pure, or nearly pure, CO_2. It has been suggested that it may be economically favorable to co-store CO_2 along with H_2S, SO_2, or NO_2. Since only a few scientific studies have evaluated the impacts of these added constituents on storage performance or risks, they are not addressed comprehensively here Moreover,the limited information gained from practical experience with acid gas injection in Canada is insufficient to assess the impacts of the added components on storage security.

Existing and planned CO_2 projects

A number of pilot and commercial CO_2 storage projects are under way or proposed (Figure 5.1). To date, most actual or planned commercial projects are associated with major gas production facilities that have gas streams containing CO_2 in the range of 10-15% by volume, such as Sleipner in the North Sea, Snohvit in the Barents Sea, In Salah in Algeria, and Gorgon in Australia (Figure 5.1), as well as the acid gas injection projects in Canada and the United States. At the Sleipner Project, operated by Statoil, over 7 $MtCO_2$ has been injected into a deep subsea saline formation since 1996 (Box 5.1). Existing and planned storage projects are also listed in Table 5.1.

Table 5.1. A selection of current and planned geological storage projects.

Box 5.1. The Sleipner Project, North Sea.

The Sleipner Project, operated by Statoil in the North Sea about 250 km off the coast of Norway, is the first commercial-scale project dedicated to geological CO_2 storage in a saline formation. The CO_2 (about 9%) from Sleipner West Gas Field is separated, then injected into a large, deep, saline formation 800 m below the seabed of the North Sea. The Saline Aquifer CO_2 Storage (SACS) project was established to monitor and research the storage of CO_2. From 1995, the IEA GHG R&D Program has worked with Statoil to arrange the monitoring and research activities. Approximately 1 $MtCO_2$ is removed from the produced natural gas and injected underground annually in the field. The CO_2 injection operation started in October 1996, and, by early 2005, more than 7 Mt CO_2 had been injected at a rate of approximately 2,700 tonnes per day. Over the lifetime of the project, a total of 20 $MtCO_2$ is expected to be stored. A simplified diagram of the Sleipner scheme is given in Figure 5.4.

The saline formation into which the CO_2 is injected is a brine-saturated unconsolidated sandstone about 800 to 1,000 m below the sea floor. The formation also contains secondary thin shale layers, which influence the internal movement of injected CO_2. The saline formation has a very large storage capacity, on the order of 1 to 10 $GtCO_2$. The top of the formation is fairly flat on a regional

scale, although it contains numerous small, low-amplitude closures. The overlying primary seal is an extensive, thick, shale layer.

This project is being carried out in three phases. Phase-0 involved baseline data gathering and evaluation, which was completed in November 1998. Phase-1 involved establishment of project status after three years of CO_2 injection. There are five main project areas regarding description of reservoir geology, reservoir simulation, geochemistry, assessment of need and cost for monitoring wells, and geophysical modelling. Phase-2, involving data interpretation and model verification, began in April 2000.

The fate and transport of the CO_2 plume in the storage formation has been monitored successfully by seismic time-lapse surveys (Figure 5.16). The surveys also show that the caprock is an effective seal that prevents CO_2 migration out of the storage formation. Today, the footprint of the plume at Sleipner extends over an area of approximately 5 km^2. Reservoir studies and simulations covering hundreds to thousands of years have shown that CO_2 will eventually dissolve in the pore water, which will become heavier and sink, thus minimizing the potential for long-term leakage (Lindeberg and Bergmo, 2003).

Figure 5.4. Simplified diagram of the Sleipner CO_2 Storage Project. Inset: location and extent of the Utsira formation.

At the In Salah Gas Field in Algeria, Sonatrach, BP, and Statoil inject CO_2 stripped from natural gas into the gas reservoir outside the boundaries of the gas field (Box 5.2). Statoil is planning another project in the Barents Sea, where CO_2 from the Snohvit field will be stripped from the gas and injected into a geological formation below the gas field. Chevron is proposing to produce gas from the Gorgon field off Western Australia, containing approximately 14% CO_2. The CO_2 will be injected into the Dupuy Formation at Barrow Island (Oen, 2003). In The Netherlands, CO_2 is being injected at pilot scale into the almost depleted K12-B offshore gas field (van der Meer et al., 2005).

Box 5.2. The In Salah, Algeria, CO_2 Storage Project.

The In Salah Gas Project, a joint venture among Sonatrach, BP, and Statoil located in the central Saharan region of Algeria, is the world's first large-scale CO_2 storage project in a gas reservoir (Riddiford et al., 2003). The Krechba Field at In Salah produces natural gas containing up to 10% CO_2 from several geological reservoirs and delivers it to markets in Europe, after processing and stripping the CO_2 to meet commercial specifications. The project involves re-injecting the CO_2 into a sandstone reservoir at a depth of 1,800 m and storing up to 1.2 $MtCO_2$ per year. Carbon dioxide injection started in April 2004, and over the life of the project, it is estimated that 17 $MtCO_2$ will be geologically stored. The project consists of 4 production and 3 injection wells (Figure 5.5). Long reach (up to 1.5 km) horizontal wells are used to inject CO_2 into the 5 md permeability reservoir.

The Krechba Field is a relatively simple anticline. Carbon dioxide injection takes place down-dip from the gas/water contact in the gas-bearing reservoir. The injected CO_2 is expected to eventually migrate into the area of the current gas field after depletion of the gas zone. The field has been mapped using 3D seismic and well data from the field. Deep faults have been mapped, but at shallower levels, the structure is unfaulted. The storage target in the reservoir interval therefore carries minimal structural uncertainty or risk. The top seal is a thick succession of mudstones up to 950 m thick.

A preliminary risk assessment of CO_2 storage integrity has been carried out, and baseline data acquired. Processes that could result in CO_2 migration from the injection interval have been quantified, and a monitoring program is planned involving a range of technologies, including noble gas tracers, pressure surveys, tomography, gravity baseline studies, microbiological studies, 4D seismic, and geomechanical monitoring.

Figure 5.5. Schematic of the In Salah Gas Project, Algeria. One $MtCO_2$ will be stored annually in the gas reservoir. Long- reach horizontal wells with slotted intervals of up to 1.5 km are used to inject CO_2 into the water-filled parts of the gas reservoir.

There are 44 CO_2-rich acid gas injection projects currently operating in western Canada, ongoing since the early 1990s (Bachu and Haug, 2005). Although mostly small scale, they provide important examples of effectively managing injection of CO_2 and hazardous gases such as hydrogen sulphide (Section 5.2.5).

Opportunities for enhanced oil recovery (EOR) have increased interest in CO_2 storage (Stevens et al., 2001b; Moberg et al., 2003; Moritis, 2003; Riddiford et al., 2003; Torp and Gale, 2003). Although not designed for CO_2 storage, CO_2-EOR projects can demonstrate associated storage of CO_2, although lack of comprehensive monitoring of EOR projects (other than at the International Energy Agency Greenhouse Gas (IEA GHG) Weyburn Project in Canada) makes it difficult to quantify storage. In the United States, approximately 73 CO_2-EOR operations inject up to 30 $MtCO_2$ per year, most of which comes from natural CO_2 accumulations—although approximately 3 $MtCO_2$ is from anthropogenic sources, such as gas processing and fertilizer plants (Stevens et al., 2001b). The SACROC project was the first large-scale commercial CO_2-EOR project in the world. It used anthropogenic CO_2 during the period from 1972 to 1995. The Rangely Weber project (Box 5.6) injects anthropogenic CO_2 from a gas-processing plant in Wyoming.

In Canada, a CO_2-EOR project has been established by EnCana at the Weyburn Oil Field in Southern Saskatchewan (Box 5.3). The project is expected to inject 23 $MtCO_2$ and extend the life of the oil field by 25 years (Moberg et al., 2003; Law, 2005). The fate of the injected CO_2 is being closely monitored through the IEA GHG Weyburn Project (Wilson and Monea, 2005). Carbon dioxide-EOR is under consideration for the North Sea, although there is as yet little, if any, operational experience for offshore CO_2-EOR. Carbon dioxide-EOR projects are also currently under way in a number of countries including Trinidad, Turkey, and Brazil (Moritis, 2002). Saudi Aramco, the world's largest producer and exporter of crude oil, is evaluating the technical feasibility of CO_2-EOR in some of its Saudi Arabian reservoirs.

In addition to these commercial storage or EOR projects, a number of pilot storage projects are under way or planned. The Frio Brine Project in Texas, U.S.A., involved injection and storage of 1,900 tonnes of CO_2 in a highly permeable formation with a regionally extensive shale seal (Hovorka et al., 2005). Pilot projects are proposed for Ketzin, west of Berlin, Germany, for the Otway Basin of South Eastern Australia, and for Teapot Dome, Wyoming, U.S.A. (Figure 5.1). The American FutureGen project, proposed for late this decade, will be a geological storage project linked to coal-fired electricity generation. A small-scale CO_2 injection and monitoring project is being carried out by RITE at Nagoaka in northwest Honshu, Japan. Small-scale injection projects to test CO_2 storage in coal have been carried out in Europe (RECOPOL) and Japan (Yamaguchi et al., 2005). A CO_2-enhanced CBM (ECBM) recovery demonstration project has been undertaken in the northern San Juan Basin of New Mexico, U.S.A. (Reeves, 2003a) (Box 5.7). Further CO_2-ECBM projects are under consideration for China, Canada, Italy, and Poland (Gale, 2003). In all, some 59

opportunities for CO_2-ECBM have been identified worldwide, the majority in China (van Bergen et al., 2003a).

These projects (Figure 5.1, Table 5.1) demonstrate that subsurface injection of CO_2 is not something for the distant future, but is being implemented now for environmental and/or commercial reasons.

Box 5.3. The Weyburn CO_2-EOR Project.

The Weyburn CO_2-enhanced oil recovery (CO_2-EOR) project is located in the Williston Basin, a geological structure extending from south central Canada into the north central United States. The project aims to permanently store almost all of the injected CO_2 by eliminating the CO_2 that would normally be released during the end of the field life.

The source of the CO_2 for the Weyburn CO_2-EOR Project is the Dakota Gasification Company facility, located approximately 325 km south of Weyburn in Beulah, North Dakota, U.S.A. At the plant, coal is gasified to make synthetic gas (methane), with a relatively pure stream of CO_2 as a by-product. This CO_2 stream is dehydrated, compressed, and piped to Weyburn in southeastern Saskatchewan, Canada, for use in the field. The Weyburn CO_2-EOR Project is designed to take CO_2 from the pipeline for a period of approximately 15 years, with delivered volumes dropping from 5,000 tonnes per day to about 3,000 tonnes per day over the life of the project.

The Weyburn field covers an area of 180 km^2, with original oil in place on the order of 222 million m^3 (1,396 million barrels). Over the life of the CO_2-EOR project (20-25 years), it is expected that some 20 $MtCO_2$ will be stored in the field, using current economics and oil recovery technology. The oil field layout and operation is relatively conventional for oil field operations. The field has been designed with a combination of vertical and horizontal wells to optimize the sweep efficiency of the CO_2. In all cases, production and injection strings are used within the wells to protect the integrity of the casing of the well.

The oil reservoir is a fractured carbonate, 20 to 27 m thick. The primary upper seal for the reservoir is an anhydrite zone. At the northern limit of the reservoir, the carbonate thins against a regional unconformity. The basal seal is also anhydrite, but is less consistent across the area of the reservoir. A thick, flat-lying shale above the unconformity forms a good regional barrier to leakage from the reservoir. In addition, several high-permeability formations containing saline groundwater would form good conduits for lateral migration of any CO_2 that might reach these zones, with rapid dissolution of the CO_2 in the formation fluids.

Since CO_2 injection began in late 2000, the performance of the EOR project has been largely as predicted. Currently, some 1,600 m^3 (10,063 barrels) per day of incremental oil is being produced from the field. All produced CO_2 is captured and recompressed for reinjection into the production zone. At the moment, some 1,000 tonnes per day of CO_2 is reinjected; this will increase as the project matures. Monitoring is extensive, with high-resolution seismic surveys and surface monitoring to determine any potential leakage. Surface monitoring includes sampling and analysis of potable groundwater, as well as soil gas sampling and analysis (Moberg et al., 2003). To date, there has been no indication of CO_2 leakage to the surface and near-surface environment (White, 2005; Strutt et al., 2003).

5.1.2 Key questions

In the previous section, the point is made that deep injection of CO_2 is under way in a number of places (Figure 5.1.) However, if CO_2 storage is to be undertaken on the scale necessary to make deep cuts to atmospheric CO_2 emissions, there must be hundreds and perhaps even thousands of large-scale geological storage projects under way worldwide. The extent to which this is, or might be, feasible depends on the answers to the key questions outlined below, and addressed subsequently in this chapter:

- How is CO_2 stored underground? What happens to the CO_2 when it is injected? What are the physico-chemical and chemical processes involved? And what are the geological controls? (Sections 5.2 and 5.3)
- How long can CO_2 remain stored underground? (Section 5.2)
- How much and where can CO_2 be stored in the subsurface, locally, regionally, globally? Is it a modest niche opportunity or is the total storage capacity sufficient to contain a large proportion of the CO_2 currently emitted to the atmosphere? (Section 5.3)
- Are there significant opportunities for CO_2-enhanced oil and gas recovery? (Section 5.3)
- How is a suitable storage site identified and what are its geological characteristics? (see Section 5.4)
- What technologies are currently available for geological storage of CO_2? (Section 5.5)
- Can we monitor CO_2 once it is geologically stored? (Section 5.6)
- Will a storage site leak and what would be the likely consequences? (Sections 5.6 and 5.7)
- Can a CO_2 storage site be remediated if something does go wrong? (Sections 5.6 and 5.7)
- Can a geological storage site be operated safely and if so, how? (Section 5.7)
- Are there legal and regulatory issues for geological storage, and a legal/regulatory framework that enables it to be undertaken? (Section 5.8)
- What is the likely cost of geological storage of CO_2? (Section 5.9)
- After reviewing our current state of knowledge, are there things that we still need to know? What are these gaps in knowledge? (Section 5.10).

The remainder of this chapter seeks to address these important questions.

5.2 Storage Mechanisms and Storage Security

Geological formations in the subsurface are composed of transported and deposited rock grains, organic material, and minerals that form after the rocks are deposited. The pore space between grains or minerals is occupied by fluid (mostly water, with proportionally minute occurrences of oil and gas). Open fractures and cavities are also filled with fluid. Injection of CO_2 into the pore space and fractures of a permeable formation can displace the *in situ* fluid, or the CO_2 may dissolve in or mix with the fluid, or react with the mineral grains, or there may be some combination of these processes. This section examines these processes and their influence on geological storage of CO_2.

5.2.1 CO_2 flow and transport processes

Injection of fluids into deep geological formations is achieved by pumping fluids down into a well (see Section 5.5). The part of the well in the storage zone is either perforated or covered with a permeable screen to enable the CO_2 to enter the formation. The perforated or screened interval is usually on the order of 10 to 100 m thick, depending on the permeability and thickness of the formation. Injection raises the pressure near the well, allowing CO_2 to enter the pore spaces initially occupied by the *in situ* formation fluids. The amount and spatial distribution of pressure buildup in

the formation will depend on the rate of injection, the permeability and thickness of the injection formation, the presence or absence of permeability barriers within it, and the geometry of the regional underground water (hydrogeological) system.

Once injected into the formation, the primary flow and transport mechanisms that control the spread of CO_2 include:

- Fluid flow (migration) in response to pressure gradients created by the injection process
- Fluid flow in response to natural hydraulic gradients
- Buoyancy caused by the density differences between CO_2 and the formation fluids
- Diffusion
- Dispersion and fingering caused by formation heterogeneities and mobility contrast between CO_2 and formation fluid
- Dissolution into the formation fluid
- Mineralization
- Pore space (relative permeability) trapping
- Adsorption of CO_2 onto organic material.

The rate of fluid flow depends on the number and properties of the fluid phases present in the formation. When two or more fluids mix in any proportion, they are referred to as miscible fluids. If they do not mix, they are referred to as immiscible. The presence of several different phases may decrease the permeability, and slow the rate of migration. If CO_2 is injected into a gas reservoir, a single miscible fluid phase consisting of natural gas and CO_2 is formed locally. When CO_2 is injected into a deep saline formation in a liquid or liquid-like supercritical dense phase, it is immiscible in water. Carbon dioxide injected into an oil reservoir may be miscible or immiscible, depending on the oil composition and the pressure and temperature of the system (Section 5.3.2). When CO_2 is injected into coal beds, in addition to some of the processes listed above, adsorption and desorption of gases (particularly methane) previously absorbed on the coal take place, as well as swelling or shrinkage of the coal itself (Section 5.3.4).

Because supercritical CO_2 is much less viscous than water and oil (by an order of magnitude or more), migration is controlled by the contrast in mobility of CO_2 and the *in situ* formation fluids (Nordbotten et al., 2005a; Celia et al., 2005). Because of the comparatively high mobility of CO_2, only some of the oil or water will be displaced, leading to an average saturation of CO_2 in the range of 30-60%. Viscous fingering can cause CO_2 to bypass much of the pore space, depending on the heterogeneity and anisotropy of rock permeability (van der Meer, 1995; Ennis-King and Paterson, 2001; Flett et al., 2005). For natural gas reservoirs, CO_2 is more viscous than natural gas, so the "front" will be stable and viscous fingering limited.

The magnitude of the buoyancy forces that drive vertical flow depends on the type of fluid in the formation. In saline formations, the comparatively large density difference (30-50%) between CO_2 and formation water creates strong buoyancy forces that drive CO_2 upwards. In oil reservoirs, the density difference and buoyancy forces are not as large, particularly if the oil and CO_2 are miscible (Kovscek, 2002). In gas reservoirs, the opposite effect will occur, with CO_2 migrating downwards under buoyancy forces, because CO_2 is denser than natural gas (Oldenburg et al., 2001).

In saline formations and oil reservoirs, the buoyant plume of injected CO_2 migrates upwards, but not evenly. This is because a lower-permeability layer acts as a barrier and causes the CO_2 to migrate laterally, filling any stratigraphic or structural trap it encounters. The shape of the CO_2 plume rising through the rock matrix (Figure 5.6) is strongly affected by formation heterogeneity, such as low-permeability shale lenses (Flett et al., 2005). Low-permeability layers within the

storage formation therefore have the effect of slowing the upward migration of CO_2, which would otherwise cause CO_2 to bypass deeper parts of the storage formation (Doughty et al., 2001).

Figure 5.6. Simulated distribution of CO_2 injected into a heterogeneous formation with low permeability layers that block upwards migration of CO_2. (a) Illustration of a heterogeneous formation facies grid model. The location of the injection well is indicated by the line in the lower portion of the grid. (b) The CO_2 distribution after 2 years of injection. Note that the simulated distribution of CO_2 is strongly influenced by the low permeability layers. These block and delay upward movement of CO_2 (after Doughty and Pruess, 2004).

As CO_2 migrates through the formation, some of it will dissolve into the formation water. In systems with slowly flowing water, reservoir-scale numerical simulations show that, over tens of years, a significant amount, up to 30% of the injected CO_2, will dissolve in formation water (Doughty et al., 2001). Basin-scale simulations suggest that over centuries, the entire CO_2 plume dissolves in formation water (McPherson and Cole, 2000; Ennis-King et al., 2003). If the injected CO_2 is contained in a closed structure (no flow of formation water), it will take much longer for CO_2 to completely dissolve because of reduced contact with unsaturated formation water. Once CO_2 is dissolved in the formation fluid, it migrates along with the regional groundwater flow. For deep sedimentary basins characterized by low permeability and high salinity, groundwater flow velocities are very low, typically on the order of millimeters to centimeters per year (Bachu et al., 1994). Thus, migration rates of dissolved CO_2 are substantially lower than for separate-phase CO_2.

Water saturated with CO_2 is slightly denser (approximately 1%) than the original formation water, depending on salinity (Enick and Klara, 1990; Bachu and Adams, 2003), and with high vertical permeability, this may lead to free convection, replacing the CO_2-saturated water from the plume vicinity with unsaturated water, producing faster rates of CO_2 dissolution (Lindeberg and Wessel-Berg, 1997; Ennis-King and Paterson, 2003). Figure 5.7 illustrates the formation of convection cells and dissolution of CO_2 over several thousand years. The solubility of CO_2 in brine decreases with increasing pressure, decreasing temperature, and increasing salinity (Appendix 1). Calculations indicate that, depending on the salinity and depth, from 20 to 60 kg CO_2 can dissolve in one cubic meter of formation fluid (Holt et al., 1995; Koide et al., 1995). With the use of a homogeneous model rather than a heterogeneous one, the time required for complete CO_2 dissolution may be underestimated.

Figure 5.7. Radial simulations of carbon dioxide injection into a homogeneous formation 100m thick, at a depth of 1 km, where the pressure is 10 MPa and the temperature is 40°C. The injection rate is 1 $MtCO_2$ per year for 20 years, the horizontal permeability is $10^{(-13)}$ m^2 (approximately 100 mD), and the vertical permeability is one tenth of that. The residual CO_2 saturation is 20%. The first three parts of the figure at 2, 20 and 200 years show the gas saturation in the porous medium, while the second three parts of the figure at 200, 2000 and 4000 years show the mass fraction of dissolved carbon dioxide in the aqueous phase (after Ennis-King and Paterson, 2003).

As CO_2 migrates through a formation, some of it is retained in the pore space by capillary forces (Figure 5.6), commonly referred to as "residual CO_2 trapping," which may immobilize significant amounts of CO_2 (Obdam et al., 2003; Kumar et al., 2005). Figure 5.8 illustrates that when the degree of trapping is high, and CO_2 is injected at the bottom of a thick formation, all of the CO_2 may be trapped by this mechanism, even before it reaches the caprock at the top of the formation. While it is formation specific, Holtz (2002) has demonstrated that residual CO_2 saturations may be as high as 15 to 25% for many typical storage formations. Over time, much of the trapped CO_2

dissolves in the formation water (Ennis-King and Paterson, 2003), although appropriate reservoir engineering can accelerate or modify solubility trapping (Keith et al., 2005).

Figure 5.8. Simulation of 50 years of injection of CO_2 into the base of a saline aquifer, capillary forces trap CO_2 in the pore space of sedimentary rocks: (a) After 50-year injection period is over most CO_2 is still mobile, driven upwards by buoyancy forces; (b) After 1000 years, buoyancy-driven flow has expanded the volume affected by CO_2, and much is trapped as residual CO_2 saturation or dissolved in brine (not shown). Little CO_2 is mobile and all CO_2 is contained within the aquifer (after Kumar et al., 2005).

5.2.2 CO_2 storage mechanisms in geological formations

The effectiveness of geological storage depends on a combination of physical and geochemical trapping mechanisms (Figure 5.9). The most effective storage sites are those where CO_2 is immobile because it is trapped permanently under a thick, low-permeability seal, or is converted to solid minerals, or is adsorbed on the surfaces of coal micropores, or through a combination of physical and chemical trapping mechanisms.

Figure 5.9. Storage security depends on a combination of physical and geochemical trapping. Over time, the physical process of residual CO_2 trapping, and geochemical processes of solubility trapping and mineral trapping increase.

5.2.2.1 Physical trapping: stratigraphic and structural

Initially, physical trapping of CO_2 below low-permeability seals (caprocks), such as very-low-permeability shale or salt beds, is the principal means to store CO_2 in geological formations (Figure 5.3). In some high latitude areas, shallow gas hydrates may conceivably act as a seal. Sedimentary basins have such closed, physically bound traps or structures, which are occupied mainly by saline water, oil, and gas. Structural traps include those formed by folding or fracturing rocks Faults can act as permeability barriers in some circumstances and as preferential pathways for fluid flow in other circumstances (Salvi et al., 2000). Stratigraphic traps are formed by changes in rock type caused by variation in the setting where the rocks were deposited. Both of these types of traps are suitable for CO_2 storage, although, as discussed in Section 5.5, care must be taken not to exceed the allowable overpressure to avoid fracturing the caprock or re-activating faults (Streit et al., 2005).

5.2.2.2 Physical trapping: hydrodynamic

Hydrodynamic trapping can occur in saline formations that do not have a closed trap, but where fluids migrate very slowly over long distances. When CO_2 is injected into a formation, it displaces saline formation water and then migrates buoyantly upwards, because it is less dense than the water. When it reaches the top of the formation, it continues to migrate as a separate phase, until it is trapped as residual CO_2 saturation or in local structural or stratigraphic traps within the sealing formation. In the longer term, significant quantities of CO_2 dissolve in the formation water and then migrate with the groundwater. Where the distance from the deep injection site to the end of the overlying impermeable formation is hundreds of kilometers, the time scale for fluid to reach the surface from the deep basin can be millions of years (Bachu et al., 1994).

5.2.2.3 Geochemical trapping

Carbon dioxide in the subsurface can undergo a sequence of geochemical interactions with the rock and formation water, which will further increase storage capacity and effectiveness. First, when

CO_2 dissolves in formation water, a process commonly called solubility trapping occurs. The primary benefit of solubility trapping is that once CO_2 is dissolved, it no longer exists as a separate phase, thereby eliminating the buoyant forces that drive it upwards. Next, it will form ionic species as the rock dissolves, accompanied by a rise in the pH. Finally, some fraction may be converted to stable carbonate minerals (mineral trapping), the most permanent form of geological storage (Gunter et al., 1993). Mineral trapping is believed to be comparatively slow, potentially taking a thousand years or longer. Nevertheless, the permanence of mineral storage, combined with the potentially large storage capacity present in some geological settings, makes this a desirable feature of long-term storage.

Dissolution of CO_2 in formation waters can be represented by the chemical reaction

$$CO_2\,(\text{gaseous}) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+$$

The CO_2 solubility in formation water decreases as temperature and salinity increase. Dissolution is rapid when formation water and CO_2 share the same pore space, but once the formation fluid is saturated with CO_2, the rate slows and is controlled by diffusion and convection rates.

CO_2 dissolved in water produces a weak acid, which reacts with the sodium and potassium basic silicate, or calcium, magnesium, and iron carbonate, or silicate minerals in the reservoir or formation, to form bicarbonate ions by chemical reactions approximating to:

$$3\ \text{K-feldspar} + 2H_2O + 2CO_2 \leftrightarrow \text{Muscovite} + 6\ \text{Quartz} + 2K^+ + 2HCO_3^-$$

Reaction of the dissolved CO_2 with minerals can be rapid (days) in the case of some carbonate minerals, but slow (hundreds to thousands of years) in the case of silicate minerals.

Formation of carbonate minerals occurs from continued reaction of the bicarbonate ions with calcium, magnesium, and iron from silicate minerals such as clays, micas, chlorites, and feldspars present in the rock matrix (Gunter et al., 1993; 1997).

Perkins et al. (2005) estimate that over 5,000 years, all the CO_2 injected into the Weyburn Oil Field will dissolve or be converted to carbonate minerals within the storage formation. Equally importantly, they show that the caprock and overlying rock formations have an even greater capacity for mineralization. This is significant for leakage risk assessment (Section 5.7) because once CO_2 is dissolved, it is unavailable for leakage as a discrete phase. Modeling by Holtz (2002) suggests more than 60% of CO_2 is trapped by residual CO_2 trapping by the end of the injection phase (100% after 1,000 years), although laboratory experiments (Section 5.2.1) suggest somewhat lower percentages. When CO_2 is trapped at residual saturation, it is effectively immobile. However, should there be leakage through the caprock, then saturated brine may degas as it is depressurized, although, as illustrated in Figure 5.5, the tendency of saturated brine is to sink rather than to rise. Reaction of the CO_2 with formation water and rocks may result in reaction products that affect the porosity of the rock and the flow of solution through the pores. This possibility has not, however, been observed experimentally, and its possible effects cannot be quantified.

Yet another type of fixation occurs when CO_2 is preferentially adsorbed onto coal or organic-rich shales (Section 5.3.4). This has been observed in batch and column experiments in the laboratory, as well as in field experiments at the Fenn Big Valley, Canada, and the San Juan Basin, U.S.A. (Box 5.7). A rather different form of fixation can occur when CO_2 hydrate is formed in the deep ocean seafloor and onshore in permafrost regions (Koide et al., 1997).

Box 5.4. Storage security mechanisms and changes over time.

When the CO_2 is injected, it forms a bubble around the injection well, displacing the mobile water and oil both laterally and vertically within the injection horizon. The interactions between the water and CO_2 phase allow geochemical trapping mechanisms to take effect. Over time, CO_2 that is not immobilized by residual CO_2 trapping can react with in situ fluid to form carbonic acid (i.e. H_2CO_3 called solubility trapping - dominates from tens to hundreds of years). Dissolved CO_2 can eventually react with reservoir minerals if an appropriate mineralogy is encountered to form carbon-bearing ionic species (i.e. HCO_3- and$CO_3$2- called ionic trapping - dominates from hundreds to thousands of years). Further breakdown of these minerals could precipitate new carbonate minerals that would fix injected CO_2 in its most secure state (i.e. mineral trapping - dominates over thousands to millions of years).

Figure 5.10. Storage expressed as a combination of physical and geochemical trapping. Level of security is proportional to distance from origin. Dashed lines are examples of million year pathways, discussed in the text.

Four injection scenarios have been shown in Figure 5.10. Scenarios "A," "B,"and "C" show injection into hydrodynamic traps, essentially systems open to lateral flow of fluids and gas within the injection horizon. Scenario "D" represents injection into a physically restricted flow regime, similar to those of many producing and depleted oil and gas reservoirs.

In scenario "A," the injected CO_2 is never physically contained laterally. The CO_2 plume migrates within the injection horizon and is ultimately consumed via all types of geochemical trapping mechanisms, including carbonate mineralization. Mineral and ionic trapping dominate. The proportions of CO_2 stored in each geochemical trap will depend strongly on the in situ mineralogy, pore space structure and water composition.

In scenario "B," the migration of the CO_2 plume is similar to that of scenario "A," but the mineralogy and water chemistry are such that reaction of CO_2 with minerals is minor, and solubility trapping and hydrodynamic trapping dominate.

In scenario "C," the CO_2 is injected into a zone initially similar to B. However, during lateral migration the CO_2 plume migrates into a zone of physical heterogeneity in the injection horizon. This zone may be characterized by variable porosity and permeability caused by a facies change. The facies change is accompanied by a more reactive mineralogy that causes an abrupt change in path. In the final state, ionic and mineral trapping predominates.

Lastly, scenario "D" illustrates CO_2 injection into a well-constrained flow zone but, similar to scenario "B," does not have in situ fluid chemistry and mineralogy suitable for ionic or mineral trapping. The bulk of the injected CO_2 is trapped geochemically via solubility trapping and physically via stratigraphic/structural trapping.

5.2.3 Natural geological accumulations of CO_2

Natural sources of CO_2 occur, as gaseous accumulations of CO_2, CO_2 mixed with natural gas, and CO_2 dissolved in formation water (Figure 5.11). These natural accumulations have been studied in the United States, Australia, and Europe (Pearce et al., 1996; Allis et al., 2001; Stevens et al., 2003; Watson et al., 2004) as analogues for storage of CO_2, as well as for leakage from engineered storage sites. Production of CO_2 for EOR and other uses provides operational experience relevant to

CO_2 capture and storage. There are, of course, differences between natural accumulations of CO_2 and engineered CO_2 storage sites: natural accumulations of CO_2 collect over very long periods of time and at random sites, some of which might be naturally "leaky." At engineered sites, CO_2 injection rates will be rapid, and the sites will necessarily be penetrated by injection wells (Celia and Bachu, 2003; Johnson et al., 2005). Therefore, care must be taken to keep injection pressures low enough to avoid damaging the caprock (Section 5.5), and to make sure that the wells are properly sealed (Section 5.5).

Natural accumulations of relatively pure CO_2 are found all over the world in a range of geological settings, particularly in sedimentary basins, intraplate volcanic regions (Figure 5.11), and in faulted areas or in quiescent volcanic structures. Natural accumulations occur in a number of different types of sedimentary rocks, principally limestones, dolomites, and sandstones, and with a variety of seals (mudstone, shale, salt, and anhydrite) and a range of trap types, reservoir depths, and CO_2-bearing phases.

Figure 5.11. Examples of some natural accumulations of CO_2 around the world. Regions containing many occurrences are enclosed by a dashed line. Natural accumulations can be useful as analogues for certain aspects of storage and for assessing the environmental impacts of leakage. Data quality is variable and the apparent absence of accumulations in South America, southern Africa and central and northern Asia is probably more a reflection of lack of data than a lack of CO_2 accumulations.

Carbon dioxide fields in the Colorado Plateau and Rocky Mountains, U.S.A., are comparable to conventional natural gas reservoirs (Allis et al., 2001). Studies of three of these fields (McElmo Dome, St. Johns Field, and Jackson Dome) have shown that each contains 1,600 Mt, with measurable leakage (Stevens et al., 2001a). Two hundred Mt trapped in the Pisgah Anticline, northeast of the Jackson Dome, is thought to have been generated more than 65 million years ago (Studlick et al., 1990), with no evidence of leakage that provides additional evidence of long-term trapping of CO_2. Extensive studies have been undertaken on small-scale CO_2 accumulations in the Otway Basin in Australia (Watson et al., 2004) and in France, Germany, Hungary, and Greece (Pearce et al., 2003).

Conversely, some systems, typically spas and volcanic systems, are leaky and not useful analogues for geological storage. The Kileaua Volcano emits on average 4 $MtCO_2$ a year. More than 1,200 tonnes CO_2 per day (438,000 tonnes per year) leaked into the Mammoth Mountain area, California, between 1990 and 1995, with flux variations linked to seismicity (USGS, 2001b). Average flux densities of 80 to 160 tonnes CO_2 per year per m^2 are observed near Matraderecske, Hungary, but along faults, the flux density can reach approximately 6,600 tonnes per year per m^2 (Pearce et al., 2003). These high seepage rates result from release of CO_2 from faulted volcanic systems, whereas a normal baseline CO_2 flux is of the order of 10-100 gm CO_2 per m^2 per day under temperate climate conditions (Pizzino et al., 2002). Seepage of CO_2 into Lake Nyos (Cameroon) resulted in CO_2 saturation of water deep in the lake, which in 1987 produced a very large-scale and (for over 1,700 persons) ultimately fatal release of CO_2 when the lake overturned (Kling et al., 1987). The overturn of Lake Nyos (a deep, stratified tropical lake) and release of CO_2 are not representative of the seepage through wells or fractures that may occur from underground geological storage sites. Engineered CO_2 storage sites will be chosen to minimize the prospect of leakage. Natural storage and events such as Lake Nyos are not representative of geological storage for predicting seepage from engineered sites, but can be useful for studying the health, safety, and environmental effects of CO_2 leakage (Section 5.7.4).

Carbon dioxide is found in some oil and gas fields as a separate gas phase or dissolved in oil. It is relatively common in South-East Asia, China, and Australia, less common in other oil and gas provinces such as in Algeria, Russia, the Paradox Basin (United States), and the Alberta Basin (western Canada). In the North Sea and Barents Sea, there is up to 10% CO_2 in a few fields, including Sleipner and Snohvit (Figure 5.11). The La Barge natural gas field in Wyoming, U.S.A., has 3,300 Mt of gas reserves, with an average of 65% CO_2 by volume. In the Appennine region of Italy, many deep wells (1-3 km depth) have trapped gas containing 90% or more of CO_2 by volume. Major CO_2 accumulations around the South China Sea include the world's largest known CO_2 accumulation, the Natuna D Alpha field in Indonesia, with 9,100 Mt plus (720 Mt natural gas. Concentrations of CO_2 can be highly variable between different fields in a basin and between different reservoir zones within the same field, reflecting complex generation, migration, and mixing processes. In Australia's Otway Basin, the timing of CO_2 input and trapping ranges between a million years and 5,000 years (Watson et al., 2004).

5.2.4 Industrial analogues for CO_2 storage

5.2.4.1 Natural Gas Storage

Underground natural gas storage projects that offer experience relevant to CO_2 storage (Lippmann and Benson, 2003; Perry, 2005) have operated successfully for almost 100 years and in many parts of the world (Figure 5.12). These projects provide for peak loads and balance seasonal fluctuations in gas supply and demand. The Berlin Natural Gas Storage Project is an example of this (Box 5.5). The majority of gas storage projects are in depleted oil and gas reservoirs and saline formations, although caverns in salt have also been used extensively. There are a number of factors critical to the success of these projects, including a suitable and adequately characterized site (permeability, thickness, and extent of storage reservoir, tightness of caprock, geological structure, lithology, etc.). Injection wells must be properly designed, installed, monitored, and maintained, and abandoned wells in and near the project must be located and plugged. Finally, taking into account a range of solubility, density, and trapping conditions, overpressuring the storage reservoir (injecting gas at a pressure that is well in excess of the *in situ* formation pressure) must be avoided.

Figure 5.12. Location of some natural gas storage projects.

Box 5.5. The Berlin Natural Gas Storage Facility.

The Berlin Natural Gas Storage Facility is located in central Berlin, Germany, in an area that combines high population density with nature and water conservation reservations. This facility, with a capacity of 1.085 billion m³, was originally designed to be a reserve natural gas storage unit for limited seasonal quantity equalization. A storage production rate of 450,000 m³ per hour can be achieved with the existing storage wells and surface facilities. Although the geological and engineering aspects and scale of the facility make it a useful analogue for a small CO_2 storage project, this project is more complex because of the high variability of input and output for natural gas, depending on consumer demand. The risk profiles are also different, considering the highly flammable and explosive nature of natural gas, and conversely the reactive nature of CO_2.

The facility lies to the east of the North German Basin, which is part of a complex of basin structures extending from The Netherlands to Poland. The sandstone storage horizons are at a depth of approximately 800 m below sea level. The gas storage layers are covered with layers of claystone, anhydrite, and halite, approximately 200 m thick. This site has complicated tectonics and heterogeneous reservoir lithologies.

Twelve wells drilled at three sites are available for the natural gas storage operation. The varying storage sand types also require different methods of completion of the wells. The wells also have major differences in their production behavior. The wellheads of the storage wells and of the water disposal wells are housed in 5m deep cellars covered with concrete plates, with special steel covers over the wellheads to allow for wireline logging. Because of the urban location, a total of 16 deviated storage wells and water disposal wells were concentrated at four sites. Facilities containing substances that could endanger water are set up within fluid-tight concrete enclosures and/or have their own watertight concrete enclosures.

While underground natural gas storage is safe and effective, some projects have leaked, mostly caused by poorly completed or improperly plugged and abandoned wells and by leaky faults (Gurevich et al., 1993; Lippmann and Benson, 2003; Perry, 2005). Abandoned oil and gas fields are easier to assess as natural gas storage sites than are saline formations, because the geological structure and caprock are usually well characterized from existing wells. At most natural gas storage sites, monitoring requirements focus on ensuring that the injection well is not leaking (by the use of pressure measurements and through *in situ* downhole measurements of temperature, pressure, noise/sonic, casing conditions etc.). Observation wells are sometimes used to verify that gas has not leaked into shallower strata.

5.2.4.2 Acid Gas Injection

Acid gas injection operations represent a commercial analogue to some aspects of geological CO_2 storage. Acid gas is a mixture of H_2S and CO_2, with minor amounts of hydrocarbon gases that can result from petroleum production or processing. In western Canada, operators are increasingly turning to acid gas disposal by injection into deep geological formations. Although the purpose of the acid gas injection operations is to dispose of H_2S, significant quantities of CO_2 are injected at the same time because it is uneconomic to separate the two gases.

Currently, regulatory agencies in western Canada approve the maximum H_2S fraction, maximum wellhead injection pressure and rate, and maximum injection volume. Acid gas is currently injected into 51 different formations at 44 different locations across the Alberta Basin, in the Canadian western provinces of Alberta and British Columbia (Figure 5.13). Carbon dioxide often represents the largest component of the injected acid gas stream, in many cases, ranging from 14% to 98% of the total volume. A total of 2.5 $MtCO_2$ and 2 Mt H_2S had been injected in western Canada by the end of 2003, at rates that varied between 840 and 500,720 m^3/day per site, with an aggregate injection rate in 2003 of 0.45 $MtCO_2$ per year and 0.55 MtH_2S per year, with no detectable leakage.

Figure 5.13. Locations of acid gas injection sites in the Alberta Basin, Canada: (a) classified by injection unit; (b) the same locations classified by rock type (from Bachu and Haug, 2005).

Acid gas injection in western Canada occurs over a wide range of formation and reservoir types, acid gas compositions, and operating conditions. Injection takes place in deep saline formations at 27 sites, into depleted oil and/or gas reservoirs at 19 sites, and into the underlying water leg of depleted oil and gas reservoirs at four sites. Carbonates form the reservoir at 29 sites, and quartz-rich sandstones dominate at the remaining 21 (Figure 5.13). In most cases, shale constitutes the overlying confining unit (caprock), with the remainder of the injection zones being confined by tight limestones, evaporites, and anhydrites.

Since the first acid-gas injection operation in 1990, 51 different injection sites have been approved,

of which 44 are currently active. One operation was not implemented, three were rescinded after a period of operation (either because injection volumes reached the approved limit or because the gas plant producing the acid gas was decommissioned), and three sites were suspended by the regulatory agency because of reservoir overpressuring.

5.2.4.3 Liquid waste injection

In many parts of the world, large volumes of liquid waste are injected into the deep subsurface every day. For example, for the past 60 years, approximately 9 billion gallons (34.1 million m^3) of hazardous waste is injected into saline formations in the United States from about 500 wells each year. In addition, over 750 billion gallons (2,843 million m^3) of oil field brines are injected from 150,000 wells each year. This combined annual U.S.A. injectate volume of about 3,000 million m^3, when converted to volume equivalent, corresponds to the volume of approximately 2GtCO_2 at a depth of 1km. Therefore, the experience gained from existing deep-fluid-injection projects is relevant in terms of the style of operation and is of a similar magnitude to that which may be required for geological storage of CO_2.

5.2.5 Security and duration of CO_2 storage in geological formations

Evidence from oil and gas fields indicates that hydrocarbons and other gases and fluids including CO_2 can remain trapped for millions of years (Magoon and Dow, 1994; Bradshaw et al., 2005). Carbon dioxide has a tendency to remain in the subsurface (relative to hydrocarbons) via its many physico-chemical immobilization mechanisms. World-class petroleum provinces have storage times for oil and gas of 5 to 100 million years, others for 350 million years, while some minor petroleum accumulations have been stored for up to 1,400 million years. However, some natural traps do leak, which reinforces the need for careful site selection (Section 5.3), characterization (Section 5.4), and injection practices (Section 5.5).

5.3 Storage Formations, Capacity, and Geographic Distribution

In this section, the following issues are addressed: In what types of geological formations can CO_2 be stored? Are such formations widespread? How much CO_2 can be geologically stored?

5.3.1 General site-selection criteria

There are many sedimentary regions in the world (Figures 2.4 to 2.6 and Figure 5.14) variously suited for CO_2 storage. In general, geological storage sites should have (1) adequate capacity and injectivity, (2) a satisfactory sealing caprock, or confining unit, and (3) a sufficiently stable geological environment to avoid compromising the integrity of the storage site. Criteria for assessing basin suitability (Bachu, 2000, 2003; Bradshaw et al., 2002) include: basin characteristics (tectonic activity, sediment type, geothermal and hydrodynamic regimes); basin resources (hydrocarbons, coal, salt), industry maturity and infrastructure; and societal issues such as level of development, economy, environmental concerns, public education and attitudes.

Figure 5.14. Distribution of sedimentary basins around the world (after Bradshaw and Dance, 2005, and USGS, 2001a). In general sedimentary basins are likely to be the most prospective areas for storage sites. However, storage sites may also be found in some areas of fold belts and in some of the highs. Shield areas constitute regions with low prospectivity for storage. The Mercator projection used here is to provide comparison with Figures 5.1, 5.8, and 5.23. The apparent dimensions of the sedimentary basins, particularly in the northern hemisphere, should not necessarily be taken as an indication of their likely storage capacity.

The suitability of sedimentary basins for CO_2 storage depends in part on their location on the continental plate. Basins formed in mid-continent locations, or near the edge of stable continental plates, are excellent targets for long-term CO_2 storage because of their stability and structure. Such basins are found within most continents and around the Atlantic, Arctic, and Indian Oceans. The storage potential of basins found behind mountains formed by plate collision is likely to be good, and these include the Rocky Mountain, Appalachian, and Andean basins in the Americas, European basins immediately north of the Alps and Carpathians, and west of the Urals, and those located south of the Zagros and Himalayas in Asia. Basins located in tectonically active areas, such as those around the Pacific Ocean or the northern Mediterranean may be less suitable for CO_2 storage, and sites in these regions must be selected carefully because of the potential for CO_2 leakage (Chiodini et al., 2001; Granieri et al., 2003). Basins located on the edges of plates where subduction is occurring, or between active mountain ranges, are likely to be strongly folded and faulted, and provide less certainty for storage. However, basins must be assessed on an individual basis. For example, the Los Angeles Basin and Sacramento Valley in California, where significant hydrocarbon accumulations have been found, have demonstrated good local storage capacity. Poor CO_2 storage potential is likely to be exhibited by basins that (1) are thin (≤1,000 m), (2) have poor reservoir and seal relationships, (3) are highly faulted and fractured, (4) are within fold belts, (5) have strongly discordant sequences, (6) have undergone significant diagenesis, or (7) have overpressured reservoirs.

The efficiency of CO_2 storage in geological media, defined as the amount of CO_2 stored per unit volume (Brennan and Burruss, 2003), increases with increasing CO_2 density. Storage safety also increases with increasing density, as buoyancy, which drives upward migration, is stronger for a lighter fluid. Density increases significantly with depth while CO_2 is in gaseous phase, increases only slightly or levels off after passing from the gaseous phase into the dense phase, and may even decrease with a further increase in depth, depending on the temperature gradient (Ennis-King and Paterson, 2001; Bachu, 2003). “Cold” sedimentary basins, characterized by low temperature gradients, are more favorable for CO_2 storage (Bachu, 2003), because CO_2 attains higher density at shallower depths (700 to 1,000 m) than in “warm” sedimentary basins, characterized by high temperature gradients where dense-fluid conditions are reached at greater depths (1,000 to 1,500 m). The depth of the storage formation (leading to increased drilling and compression costs for deeper formations) may also influence the selection of storage sites.

Adequate porosity and thickness (for storage capacity) and permeability (for injectivity) are critical; porosity usually decreases with depth because of compaction and cementation, which reduces storage capacity and efficiency. The storage formation should be capped by extensive confining units (such as shale, salt, or anhydrite beds) to ensure that CO_2 does not escape into overlying, shallower rock units and ultimately to the surface. Extensively faulted and fractured sedimentary basins or parts thereof, particularly in seismically active areas, require careful characterization to be good candidates for CO_2 storage, unless the faults and fractures are sealed and CO_2 injection will not open them (Holloway, 1997; Zarlenga et al., 2004).

The pressure and flow regimes of formation waters in a sedimentary basin are important factors in selecting sites for CO_2 storage (Bachu et al., 1994). Injection of CO_2 into formations overpressured by compaction and/or hydrocarbon generation may raise technological and safety issues that make them unsuitable. Underpressured formations in basins located mid-continent, near the edge of stable continental plates, or behind mountains formed by plate collision may be well suited for CO_2 storage. Storage of CO_2 in deep saline formations with fluids having long residence times (millions of years) is conducive to hydrodynamic and mineral trapping (Section 5.2).

The possible presence of fossil fuels and the exploration and production maturity of a basin are additional considerations for selection of storage sites (Bachu, 2000). Basins with little exploration for hydrocarbons may be uncertain targets for CO_2 storage, because of limited availability of geological information or potential for contamination of as-yet-undiscovered hydrocarbon resources. Mature sedimentary basins may be prime targets for CO_2 storage because: (1) they have well-known characteristics; (2) hydrocarbon pools and/or coal beds have been discovered and produced; (3) some petroleum reservoirs might be already depleted, nearing depletion, or abandoned as uneconomic; (4) the infrastructure needed for CO_2 transportation and injection may already be in place. The presence of wells penetrating the subsurface in mature sedimentary basins can create potential CO_2 leakage pathways that may compromise the security of a storage site (Celia and Bachu, 2003). Nevertheless, despite the presence of many hundreds of existing wells, after four years of CO_2 injection there has been no measurable leakage at Weyburn (Strutt et al., 2003).

5.3.2 Oil and gas fields

5.3.2.1 Abandoned oil and gas fields

Depleted oil and gas reservoirs are prime candidates for CO_2 storage for several reasons. First, the oil and gas that originally accumulated in traps (structural and stratigraphic) did not escape (in some cases for many millions of years), demonstrating their integrity and safety. Second, the geological structure and physical properties of most oil and gas fields have been extensively studied and characterized. Third, computer models have been developed in the oil and gas industry to predict the movement, displacement behavior, and trapping of hydrocarbons. Finally, some of the infrastructure and wells already in place may be used for handling CO_2 storage operations. Depleted fields will not be adversely affected by CO_2 (having already contained hydrocarbons), and if hydrocarbon fields are still in production, a CO_2 storage scheme can be optimized to enhance oil (or gas) production. However, plugging of abandoned wells in many mature fields began many decades ago, when wells were simply filled with a mud-laden fluid. Subsequently, cement plugs were required to be strategically placed within the wellbore, but not with any consideration that they may one day be relied upon to contain a reactive and potentially buoyant fluid such as CO_2. Therefore, the condition of wells penetrating the caprock must be assessed (Winter and Bergman, 1993). In many cases, even locating the wells may be difficult, and caprock integrity may need to be confirmed by pressure and tracer monitoring.

The capacity of a reservoir will be limited by the need not to exceed pressures that damage the caprock (Section 5.5.4). Reservoirs should have limited sensitivity to reductions in permeability caused by plugging of the near-injector region and reservoir stress fluctuations (Kovscek, 2002; Bossie-Codreanu et al., 2003). Storage in reservoirs at depths less than approximately 800 m may be technically and economically feasible, but the low storage capacity of shallow reservoirs, where CO_2 may be in the gas phase, could be problematic.

5.3.2.2 Enhanced Oil Recovery

Enhanced oil recovery (EOR) through CO_2 flooding (by injection) offers potential economic gain from incremental oil production. Between 5 and 40% of the original oil in place is usually recovered by conventional primary production (Holt et al., 1995). An additional 10 to 20% of oil in place is produced by secondary recovery using water flooding (Bondor, 1992). Various miscible

agents, among them CO_2, have been used for enhanced (tertiary) oil recovery, or EOR, with an incremental oil recovery ranging from 7 to 23% (average 13.2%) of the original oil in place (Martin and Taber, 1992; Moritis, 2003). Descriptions of CO_2-EOR projects are provided in Box 5.3 and Box 5.6.

Box 5.6. The Rangely, Colorado, CO_2-EOR Project.

The Rangely CO_2-EOR Project is located in Colorado, United States, and is operated by Chevron. The CO_2 is purchased from the Exxon-Mobil LaBarge natural gas processing facility in Wyoming and transported 283 km via pipeline to the Rangely field. Additional spurs carry CO_2 over 400 km from LaBarge to Lost Soldier and Wertz fields in central Wyoming, currently ending at Salt Creek field in eastern Wyoming.

The sandstone reservoir of the Rangely field has been CO_2 flooded, using the water alternating gas (WAG) process, since 1986. Primary and secondary recovery, carried out between 1944 and 1986, recovered 1.9 billion barrels of oil (21% of the original oil in place). Using CO_2 floods, ultimate tertiary recovery of a further 129 million barrels of oil (6.8% of original oil in place) is expected. Average daily CO_2 injection in 2003 was equivalent to 2.97 $MtCO_2$ per year, with production of 13,913 barrels oil per day. Of the total 2.97 Mt injected, recycled gas comprised around 2.29 Mt and purchased gas about 0.74 Mt. Cumulative CO_2 stored to date is estimated at 22.2 Mt. A simplified flow diagram for the Rangely field is given in Figure 5.15.

The Rangely field, covering an area of 78 km^2, is an asymmetric anticline. A major northeast-to-southwest fault in the eastern half of the field and other faults and fractures significantly influence fluid movement within the reservoir. The sandstone reservoirs have an average gross and effective thickness of 160 m and 40 m respectively, comprised of six persistent producing sandstone horizons (depths between 1,675 to 1,980 m) with average porosity of 12%. Permeability averages 10 md (Hefner and Barrow, 1992).

By the end of 2003, there were 248 active injectors, of which 160 are used for CO_2 injection, and 348 active producers. Produced gas is processed through two parallel single-column natural-gas-liquids recovery facilities and subsequently compressed to approximately 14.5 MPa. Compressed-produced gas (recycled gas) is combined with purchased CO_2 for reinjection using mostly WAG process.

Carbon dioxide-EOR operation in the field maintains compliance with government regulations for production, injection, protection of potable water formations, surface use, flaring, and venting. A number of protocols have been instituted to ensure containment of CO_2—e.g., pre-injection well-integrity verification, a radioactive tracer survey run on the first injection, injection-profile tracer surveys, mechanical integrity tests, soil gas survey, round-the-clock field monitoring. Surface release from the storage reservoir is below the detection limit of 170 tonne per year, or an annual leakage rate of less than 0.00076% of the total stored CO_2 (Klusman, 2003). Methane leakage is estimated to be 400 tonnes per year, possibly due to increased CO_2 injection pressure above original reservoir pressure. The water chemistry portion of the study indicates that the injected CO_2 is dissolving in the water and may be responsible for dissolution of ferroan calcite and dolomite. There is currently no evidence of mineral precipitation that may result in mineral storage of CO_2.

Figure 5.15. Injection of CO_2 for enhanced oil recovery (EOR) with some storage of retained CO_2 (after IEA Greenhouse Gas R&D Programme). The CO_2 that is produced with the oil is separated and reinjected back into the formation. Recycling of produced CO_2 decreases the amount of CO_2 that must be purchased and avoids emissions to the atmosphere.

Many CO_2 injection schemes have been suggested, including continuous CO_2 injection or alternate water and CO_2 gas injection (Klins and Farouq Ali, 1982; Klins, 1984). Oil displacement by CO_2 injection relies on the phase behavior of CO_2 and crude oil mixtures that are strongly dependent on reservoir temperature, pressure, and crude oil composition. These mechanisms range from oil swelling and viscosity reduction for injection of immiscible fluids (low pressures) to completely miscible displacement in high-pressure applications. In these applications, more than 50% and up to 67% of the injected CO_2 returns with the produced oil (Bondor, 1992) and is usually separated and re-injected into the reservoir to minimize operating costs. The remainder is trapped in the oil reservoir by various means, such as irreducible saturation and dissolution in reservoir oil that it is not produced and in pore space that is not connected to the flow path for the producing wells.

For enhanced CO_2 storage in EOR operations, oil reservoirs may need to meet additional criteria (Klins, 1984; Taber et al., 1997; Shaw and Bachu, 2002; Kovscek, 2002). Generally, reservoir depth must be greater than 600 m. Injection of immiscible fluids must often suffice for heavy-to-medium-gravity oils (oil gravity 12 to 25 API). The more desirable miscible flooding is applicable to light, low-viscosity oils (oil gravity 25 to 48 API). For miscible floods, the reservoir pressure must be higher than the minimum miscibility pressure (10-15 MPa) needed for achieving miscibility between reservoir oil and CO_2, depending on oil composition and gravity, reservoir temperature, and CO_2 purity (Metcalfe, 1982). Other preferred criteria for both types of flooding include relatively thin reservoirs (less than 20 m), high reservoir angle, homogenous formation, and low vertical permeability to achieve effective removal of the oil For horizontal reservoirs, the absence of natural water flow, major gas cap, and major natural fractures are preferred. Reservoir thickness and permeability are not critical factors.

Reservoir heterogeneity also affects CO_2 storage efficiency. The density difference between the lighter CO_2 and the reservoir oil and water leads to movement of the CO_2 along the top of the reservoir, particularly if the reservoir is relatively homogeneous and has high permeability, negatively affecting the CO_2 storage and oil recovery. Consequently, reservoir heterogeneity may have a positive effect, slowing down the rise of CO_2 to the top of the reservoir and forcing it to spread laterally, giving more complete invasion of the formation and greater storage potential (Bondor, 1992; Kovscek, 2002; Flett et al., 2005).

5.3.2.3 Enhanced Gas Recovery

Although up to 95% of original gas in place can be produced, CO_2 could potentially be injected into depleted gas reservoirs to enhance gas recovery through reservoir repressurization (van der Burgt et al., 1992; Oldenburg et al., 2001; Koide and Yamazaki, 2001). Enhanced gas recovery has so far only been implemented at pilot scale (Gaz de France project, Netherlands, *reference*), and some authors have suggested that CO_2 injection might result in lower gas recovery factors, particularly for very heterogeneous fields (Clemens and Wit, 2002).

5.3.3 Saline formations

Saline formations are deep sedimentary rocks saturated with formation waters or brines containing high concentrations of dissolved salts. They are widespread and contain enormous quantities of water, but are unsuitable for agriculture or human consumption. Saline brines are used locally by the chemical industry, and formation waters of varying salinity are used in health spas and for the production of low-enthalpy geothermal energy. Because the use of geothermal energy is likely to increase, potential geothermal areas may not be suitable for CO_2 storage. It has been suggested that combined geological storage and geothermal energy may be feasible, but regions with good geothermal energy potential are generally less favorable for CO_2 geological storage, because of the

high degree of faulting and fracturing and the sharp increase of temperature with depth. In very arid regions, deep saline formations may be considered for future water desalinization.

The Sleipner Project in the North Sea is the best available example of a CO_2 storage project in a saline formation (Box 5.1). It was the first commercial-scale project dedicated to geological CO_2 storage. Approximately 1 $MtCO_2$ is removed annually from the produced natural gas and injected underground at Sleipner. The operation started in October 1996, and over the lifetime of the project a total of 20 Mt CO_2 is expected to be stored. A simplified diagram of the Sleipner scheme is given in Figure 5.4.

The CO_2 is injected into poorly cemented sands about 800 to 1,000 m below the sea floor. The sandstone contains secondary thin shale or clay layers, which influence the internal movement of injected CO_2. The overlying primary seal is an extensive thick shale or clay layer. The saline formation into which CO_2 is injected has a very large storage capacity.

The fate and transport of the Sleipner CO_2 plume has been monitored successfully (Figure 5.16) by seismic time-lapse surveys (Section 5.6) and has helped improve the conceptual model for the fate and transport of stored CO_2. The vertical cross section of the plume shown in Figure 5.16 indicates both the upwards migration of CO_2 (due to buoyancy forces) as well as the role of lower-permeability strata within the formation, diverting some of the CO_2 laterally, thus spreading out the plume over a larger area. The survey also shows that the caprock prevents migration out of the storage formation. The seismic data shown in Figure 5.16 illustrate the gradual growth of the plume. Today, the footprint of the plume at Sleipner extends over an area of approximately 5 km^2. Reservoir studies and simulations (Section 5.4.2) have shown that the CO_2-saturated brine will eventually become denser and sink, thus eliminating the potential for long-term leakage (Lindeberg and Bergmo, 2003).

Figure 5.16. (a) Vertical seismic sections through the CO_2 plume in the Utsira Sand at the Sleipner gas field, North Sea, showing its development over time. Note the chimney of high CO_2 saturation (c) above the injection point (black dot) and the bright layers corresponding to high acoustic response due to CO_2 in a gas form being resident in sandstone beneath thin low-permeability horizons within the reservoir; (b) horizontal seismic sections through the developing CO_2 plume at Sleipner showing its growth over time, not available for 2002 because the CO_2 plume-specific monitoring was completed in 2001 (courtesy of Andy Chadwick and the CO2STORE project).

5.3.4 Coal seams

Coal contains fractures (cleats) that impart some permeability to the system. Between cleats, solid coal has a very large number of micropores into which gas molecules from the cleats can diffuse and be tightly adsorbed. Coal can physically adsorb many gases, and may contain up to 25 Nm^3 methane per tonne of coal at coal seam pressures. It has higher affinity to adsorb gaseous CO_2 than methane (Figure 5.17). The volumetric ratio of adsorbable CO_2:CH_4 ranges from as low as 1 for mature coals, such as anthracite, to 10 or more for younger, immature coals such as lignite. Gaseous CO_2 injected through wells will flow through the cleat system of the coal, diffuse into the coal matrix, and be adsorbed onto the coal micropore surfaces, freeing up gases with lower affinity to coal (i.e., methane).

The process of CO_2 trapping in coals for temperatures and pressures above the critical point is not well understood (Larsen, 2003). It seems that adsorption is gradually replaced by absorption and the CO_2 diffuses or "dissolves" in coal. Carbon dioxide is a "plasticizer" for coal, lowering the

temperature required to cause the transition from a glassy, brittle structure to a rubbery, plastic structure (coal softening). In one case, the transition temperature was interpreted to drop from ~400°C at 3 MPa to <30°C at 5.5 MPa CO_2 pressure (Larsen, 2003). The transition temperature is dependent on the maturity of the coal, the maceral content, the ash content, and the confining stress, and is not easily extrapolated to the field. Coal plasticization, or softening, may adversely affect the permeability that would allow CO_2 injection. Furthermore, coal swells as CO_2 is adsorbed and/or absorbed, which reduces permeability and injectivity by orders of magnitude or more (Shi and Durucan, 2005), and which may be counteracted by increasing the injection pressures (Clarkson and Bustin, 1997; Palmer and Mansoori, 1998; Krooss et al., 2002; Larsen, 2003). Some studies suggest that the injected CO_2 may react with coal (Zhang et al., 1993), further highlighting the difficulty in injecting CO_2 into low-permeability coal.

Figure 5.17. Pure gas absolute adsorption in standard cubic feet per tonne (SCF/tonne) on Tiffany Coals at 130°F (after Gasem et al., 2002).

If CO_2 is injected into coal seams, it can displace methane, thereby enhancing CBM recovery. Carbon dioxide has been injected successfully at the Allison Project (Box 5.7), and in the Alberta Basin, Canada (Gunter et al., 2005), at depths greater than that corresponding to the CO_2 critical point. Carbon dioxide-ECBM has the potential to increase the amount of produced methane to nearly 90% of the gas, compared to conventional recovery of only 50% by reservoir-pressure depletion alone (Stevens et al., 1996).

Box 5.7. The Allison Unit CO_2-ECBM Pilot.

The Allison Unit CO_2-ECBM Recovery Pilot Project, located in the northern New Mexico portion of the San Juan Basin, U.S.A., is owned and operated by Burlington Resources. Production from the Allison field began in July 1989, and CO_2 injection operations for ECBM recovery commenced in April 1995. Carbon dioxide injection was suspended in August 2001 to evaluate the results of the pilot. Since this pilot was undertaken purely for the purposes of ECBM production, no CO_2 monitoring program was implemented.

The CO_2 was sourced from the McElmo Dome in Colorado and delivered to the site through a (then) Shell (now Kinder-Morgan) CO_2 pipeline. The Allison Unit has a CBM resource of 242 million m^3 per km^2. A total of 6.4 Bcf of natural CO_2 was injected into the reservoir over six years, of which 1.6 Bcf is forecast to be ultimately produced back, resulting in a net storage volume of 277,000 tonnes of CO_2. The pilot consists of 16 methane production wells, 4 CO_2 injection wells, and one pressure observation well. The injection operations were undertaken at constant surface injection pressures on the order of 10.4 MPa.

The wells were completed in the Fruitland coal, which is capped by shale. The reservoir has a thickness of 13 m, is located at a depth of 950 m, and had an original reservoir pressure of 11.5 MPa. In a study conducted under the Coal-Seq Project performed for the U.S. Department of Energy (www.coal-seq.com), a detailed reservoir characterization and modeling of the pilot was developed using the COMET2 reservoir simulator, and future field performance was forecast under various operating conditions.

Based on the study, there is evidence of significant coal-permeability reduction with CO_2 injection. This permeability reduction resulted in a two-fold reduction in injectivity. This effect compromised incremental methane recovery and project economics. Finding ways to overcome and/or prevent this effect is therefore an important topic for future research. The injection of CO_2 at the Allison Unit has resulted in an increase in methane recovery from an estimated 77% of original gas in place

to 95% of the original gas in place within the project area. The recovery of methane was in a proportion of approximately one volume of methane for every three volumes of CO_2 injected (Reeves et al., 2004).

An economic analysis of the pilot indicated a net present value of negative U.S. $627,000, assuming a discount rate of 12% and an initial capital expenditure of $2.6 million, but not including the beneficial impact of any tax credits for production from nonconventional reservoirs. This was based on a gas price of $2.20 per MMbtu (at the time) and a CO_2 price of $0.30 per Mcf ($5.19 per tonne). The results of the financial analysis will change, based on the cost of oil and gas (the analysis indicated that the pilot would have yielded a positive net present value of $2.6 million at today's gas prices), and the cost of CO_2. It was also estimated that if injectivity had been improved by a factor of four (but still using $2.20/MMbtu), the net present value would have increased to $3.6 million. Increased injectivity and today's gas prices combined would have yielded a net present value for the pilot of $15 million, or a profit of $34 per tonne of CO_2 retained in the reservoir (Reeves et al., 2003).

Coal permeability is one of several determining factors in the selection of a storage site. Coal permeability varies widely and generally decreases with increasing depth as a result of cleat closure with increasing effective stress. Most CBM-producing wells in the world less than 1,000 m deep.

Original screening criteria proposed in selecting favorable areas for CO_2 ECBM (IEA, 1998) include:

- Adequate permeability (minimum values have not yet been determined)
- Suitable coal geometry (a few, thick seams rather than multiple, thin seams)
- Simple structure (minimal faulting and folding)
- Homogeneous and confined coal seam(s) that are laterally continuous and vertically isolated
- Adequate depth (down to 1,500 m, greater depths have not yet been studied)
- Suitable gas saturation conditions (high gas saturation for ECBM)
- Ability to dewater the formation

However, more recent studies have indicated that coal rank may play a more significant role than previously thought, owing to the dependence of relative adsorptive capacities between methane and CO_2 with coal rank (Reeves et al., 2004).

If the coal is never mined or depressurized, it is likely CO_2 will be stored for geological time, but, as with any geological storage option, disturbance of the formation could void any storage. The likely future fate of a coal seam is, therefore, a key determinant of its suitability for storage and in storage site selection, and conflicts between mining and CO_2 storage are possible, particularly for shallow coals.

5.3.5 Other geological media

Other geological media and/or structures - including basalts, oil or gas shale, salt caverns and abandoned mines - may locally provide niche options for geological storage of CO_2.

Basalts. Flows and layered intrusions of basalt occur globally, with large volumes present around the world (McGrail et al., 2003). Basalt commonly has low porosity, low permeability, and low pore space continuity, and any permeability is generally associated with fractures through which CO_2 will leak unless there is a suitable caprock. Nonetheless, basalt may have some potential for

mineral trapping of CO_2, as injected CO_2 may react with silicates in the basalt to form carbonate minerals (McGrail et al., 2003). More research is needed, but in general, basalts appear unlikely to be suitable for CO_2 storage.

Oil or Gas Rich Shale. Deposits of oil or gas shale, or organic-rich shale, occur in many parts of the world. The trapping mechanism for oil shale is similar to that for coal beds, namely CO_2 adsorption onto organic material. Carbon dioxide-enhanced shale-gas production (like ECBM) has the potential to reduce storage costs. The potential for storage of CO_2 in oil or gas shale is currently unknown, but the large volumes of shale suggest that storage capacity may be significant. If site-selection criteria, such as minimum depth, are developed and applied to these shales, then volumes could be limited, but the very low permeability of these shales is likely to preclude injection of large volumes of CO_2.

Salt Caverns. Storage of CO_2 in salt caverns created by solution mining could use the technology developed for the storage of liquid natural gas and petroleum products in salt beds and domes in western Canada and the Gulf of Mexico (Dusseault et al., 2004). A single salt cavern can reach more than 500,000 m^3. Storage of CO_2 in salt caverns differs from natural gas and compressed air storage because in the latter case, the caverns are cyclically pressurized and depressurized on a daily-to-annual time scale, whereas CO_2 storage must be effective on a centuries-to-millennia time scale. Owing to the creep properties of salt, a cavern filled with supercritical CO_2 will decrease in volume, until the pressure inside the cavern equalizes the external stress in the salt bed (Bachu and Dusseault, 2005). Although a single cavern 100 m in diameter may hold only ~0.5 Mt of high density CO_2, arrays of caverns could be built for large scale storage. Cavern sealing is important in preventing leakage and collapse of cavern roofs, which could release large quantities of gas (Katzung et al., 1996). Advantages of CO_2 storage in salt caverns include high capacity per unit volume ($kgCO_2m^{-3}$), efficiency, and injection flow rate. Disadvantages are the potential for CO_2 release in the case of system failure, the relatively small capacity of most individual caverns, and the environmental problems of disposing of brine from a solution cavity. Salt caverns can also be used for temporary storage of CO_2 in collector and distributor systems between sources and sinks of CO_2.

Abandoned Mines. The suitability of mines for CO_2 storage depends on the nature and sealing capacity of the rock in which mining occurs. Heavily fractured rock, typical of igneous and metamorphic terrains, would be difficult to seal. Mines in sedimentary rocks may offer some CO_2-storage opportunities (e.g., potash and salt mines, or stratabound lead and zinc deposits). Abandoned coal mines offer the opportunity to store CO_2, with the added benefit of adsorption of CO_2 onto coal remaining in the mined-out area (Piessens and Dusar, 2004). However, the rocks above coal mines are strongly fractured, which increases the risk of gas leakage. In addition, long-term, safe, high-pressure, CO_2-resistant shaft seals have not been developed, and any shaft failure could result in release of large quantities of CO_2. Nevertheless, in Colorado, U.S.A., there is a natural gas storage facility in an abandoned coalmine.

5.3.6 Effects of impurities on storage capacity

The presence of impurities in the CO_2 gas stream affects the engineering processes of capture, transportation, and injection (Chapters 3 and 4), as well as the trapping mechanisms and capacity for CO_2 storage in geological media. Some contaminants in the CO_2 stream (e.g., SO_X, NO_x, H_2S) may require classification as hazardous, imposing different requirements for injection and disposal than if the stream were pure (Bergman et al., 1997). Gas impurities in the CO_2 stream affect the compressibility of the injected CO_2 (and hence the volume needed for storing a given amount) and

reduce the capacity for storage in free phase, because of the storage space taken by these gases. Additionally, depending on the type of geological storage, the presence of impurities may have some other specific effects.

In EOR operations, impurities affect the oil recovery because they change the solubility of CO_2 in oil and the ability of CO_2 to vaporize oil components (Metcalfe, 1982). Methane and nitrogen decrease oil recovery, whereas hydrogen sulphide, propane, and heavier hydrocarbons have the opposite effect (Alston et al., 1985; Sebastian et al., 1985). The presence of SO_x may improve oil recovery, whereas the presence of NO_x can retard miscibility and thus reduce oil recovery (Bryant and Lake, 2005), and O_2 can react exothermally with oil in the reservoir.

In the case of CO_2 storage in deep saline formations, the presence of gas impurities affects the rate and amount of CO_2 storage through dissolution and precipitation. Additionally, leaching of heavy metals from the minerals in the rock matrix by SO_2 or O_2 contaminants is possible. Experience to date with acid gas injection (Section 5.2.5) suggests that the effect of impurities is not significant, although Knauss et al. (2005) suggest SO_x injection with CO_2 produces substantially different chemical, mobilization, and mineral reactions. There is a need for clarity about the range of gas compositions that industry might wish to store, other than pure CO_2 (Anheden et al., 2005), for while there might be environmental issues to address, there might be cost savings in co-storage of CO_2 and contaminants.

In the case of CO_2 storage in coal seams, impurities may also have a positive or negative effect, similarly to EOR operations. If a stream of gas containing H_2S or SO_2 is injected into coal beds, these will likely be preferentially adsorbed because of their higher affinity to coal than CO_2, thus reducing the storage capacity for CO_2 (Chikatamarla and Bustin, 2003). If oxygen is present, it will react irreversibly with the coal, thus reducing the sorption surface and, hence, the adsorption capacity. On the other hand, some impure CO_2 waste streams, such as coal-fired flue gas (i.e., primarily $N_2 + CO_2$), may be used for ECBM, because the CO_2 is stripped out (retained) by the coal reservoir, owing to its higher sorption selectivity compared to N_2 and CH_4.

5.3.7 Geographic distribution and storage capacity estimates

Identifying potential sites for CO_2 geological storage and estimating their capacity on a regional or local scale should conceptually be a simple task. The differences between the various mechanisms and means of trapping (Sections 5.1.2 and 5.2.2) suggest in principle the following methods:

1. For volumetric trapping, capacity is the product of available volume (pore space or cavity) and CO_2 density at *in situ* pressure and temperature.
2. For solubility trapping, capacity is the amount of CO_2 that can be dissolved in the formation fluid (oil in oil reservoirs, brackish water or brine in saline formations).
3. For adsorption trapping, capacity is the product of coal volume and its capacity for adsorbing CO_2.
4. For mineral trapping, capacity is calculated on the basis of available minerals for carbonate precipitation and the amount of CO_2 that will be used in these reactions.

The major impediments in applying these simple methods for estimating the capacity for CO_2 storage in geological media are the lack of data, their uncertainty, the resources needed to process data when available, and the fact that frequently more than one trapping mechanism is active. This leads to two situations:
Global capacity estimates have been calculated using simplifying assumptions and very simplistic methods, and hence are not reliable.

Country- and region/basin-specific estimates are more detailed and precise, but still affected by the limitations imposed by availability of data and the methodology used. Country/basin specific capacity estimates are only available for North America, Western Europe, Australia, and Japan.

The geographic distribution and capacity estimates are presented below and summarized in Table 5.2.

Table 5.2. Storage capacity for several geological storage options. The storage capacity includes storage options that are not economical.

5.3.7.1 Storage in oil and gas reservoirs

This CO_2 storage option is restricted to hydrocarbon-producing basins, which represent numerically less than half of the sedimentary provinces in the world. It is generally assumed that oil and gas reservoirs can be used for CO_2 storage after their oil or gas reserves are depleted, although storage combined with enhanced oil or gas production can occur sooner. Short of a detailed, reservoir-by-reservoir analysis, the CO_2 storage capacity can and should be calculated using databases of reserves and production (e.g., Winter and Bergman, 1993; Stevens et al., 2001b; Bachu and Shaw, 2003; 2005; Beecy and Kuuskra, 2005).

In hydrocarbon reservoirs with little water encroachment, the injected CO_2 will generally occupy the pore volume previously occupied by oil and/or natural gas. However, not all the previously (hydrocarbon-saturated) pore space will be available for CO_2, because some residual water may be trapped in the pore space due to capillarity, viscous fingering, and gravity effects (Stevens et al., 2001c). In open hydrocarbon reservoirs (where pressure is maintained by water influx), in addition to the capacity reduction caused by capillarity and other local effects, a significant fraction of the pore space will be invaded by water, decreasing the pore space available for CO_2 storage, if repressuring the reservoir is limited to preserve reservoir integrity. In western Canada, this loss was estimated to be in the order of 30% for gas reservoirs and 50% for oil reservoirs, if reservoir repressuring with CO_2 is limited to the initial reservoir pressure (Bachu et al., 2004). The capacity estimates presented here for oil and gas reservoirs have not included any "discounting" that may be appropriate for water-drive reservoirs because detailed site-specific reservoir analysis is needed to assess the effects of water-drive on capacity on a case-by-case basis.

Many storage-capacity estimates for oil and gas fields do not distinguish capacity relating to oil and gas that has already been produced, from capacity relating to remaining reserves yet to be produced and that will become available in future years. In some global assessments, estimates also attribute capacity to undiscovered oil and gas fields that might be discovered in future years. There is uncertainty about when oil and gas fields will be depleted and become available for CO_2 storage. The depletion of oil and gas fields is mostly affected by economic rather than technical considerations, particularly oil and gas prices. It is possible that production from near-depleted fields will be extended if future economic considerations allow more hydrocarbons to be recovered, thus delaying access to such fields for CO_2 storage. Currently few of the world's large oil and gas fields are depleted.

A variety of regional and global estimates of storage capacity in oil and gas fields have been made. Regional and national assessments use a "bottom-up" approach, based on field reserves data from each area's existing and discovered oil and gas fields. Although the methodologies used may differ, there is a higher level of confidence in these than the global estimates, for the reasons outlined previously. Currently, this type of assessment is only available for northwestern Europe, U.S.A., Canada, and Australia. In Europe, there have been three bottom-up attempts to estimate the CO_2

storage capacity of oil and gas reservoirs covering parts of Europe, but comprising most of Europe's storage capacity since they include the North Sea (Holloway, 1996; Wildenborg et al., 2005b). The basis of the methodology used in all three studies was that the total reservoir volume of hydrocarbons could be replaced by CO_2. The operators' estimate of "ultimately recoverable reserves" (URR) is used for each field where available, or is estimated. The underground volume occupied by the URR and the amount of CO_2 that could be stored in that space under reservoir conditions was then calculated. Undiscovered reserves were excluded. In the case of Canada, the assumption was that the produced reserves (not the original oil or gas in place) could be replaced by CO_2 (theoretical capacity) for all reservoirs in western Canada, based on *in situ* pressure, temperature, and pore volume. Reduction coefficients were then applied to account for aquifer invasion and all other effects (effective capacity). This was then reduced for depth (between 900 and 3,500 m) and size (practical capacity) (Bachu and Shaw, 2005).

The storage potential of northwestern Europe is estimated at more than 40 $GtCO_2$ for gas reservoirs and 7 $GtCO_2$ for oil fields (Wildenborg et al., 2005b). The European estimates are based on all reserves (no significant fields occur above 800 m). Carbon dioxide density was calculated from the depth, pressure, and temperature of fields in most cases; where these were not available, a density of 700 kg/m^3 was used. No assumption was made about the amount of oil recovered from the fields before CO_2 storage was initiated, and tertiary recovery by EOR is not included. In western Canada, the practical CO_2 storage potential in the Alberta and Williston basins in reservoirs with capacity greater than 1 $MtCO_2$ each is estimated at ~1 $GtCO_2$ in oil reservoirs and ~4 $GtCO_2$ in gas reservoirs. The capacity in all discovered oil and gas reservoirs is approximately 10 $GtCO_2$ (Bachu et al., 2004; Bachu and Shaw, 2005). For Canada, the CO_2 density was calculated for each reservoir based on pressure and temperature. The oil and gas recovery was that provided in the reserves databases, or based on actual production. For reservoirs suitable for EOR, an analytical method was developed to estimate how much would be produced and how much CO_2 would be stored (Shaw and Bachu, 2002). In the United States, the total storage capacity in discovered oil and gas fields is estimated to be approximately 98 $GtCO_2$ (Winter and Bergman, 1993; Bergman et al., 1997). Based on production to date and known reserves and resources, there is up to 15 $GtCO_2$ storage capacity in gas reservoirs and 0.7 $GtCO_2$ in oil reservoirs in Australia. The Australian estimates used field data to recalculate the CO_2 that could occupy the producible volume at field conditions. The total storage capacity in discovered fields for these regions with bottom-up assessments is 170 $GtCO_2$.

Although not yet assessed, it is almost certain that significant storage potential exists in all other oil and gas provinces around the world, such as the Middle East, Russia, Asia, Africa, and Latin America.

Global capacity for CO_2-EOR opportunities is estimated to have CO_2 geological storage capacity between 61 and 123 $GtCO_2$, although as practiced today, CO_2-EOR is not engineered to maximize CO_2 storage. In fact, it is optimized to maximize revenues from oil production, which in many cases requires minimizing the amount of CO_2 retained in the reservoir. In the future, if storing CO_2 has an economic value, co-optimizing CO_2 storage and EOR may increase capacity estimates. In European capacity studies, it was considered likely that EOR would be attempted at all oil fields where CO_2 storage took place, because it would generate additional revenue. The calculation in Wildenborg et al. (2005b) allows for different recovery factors based on API (American Petroleum Institute) gravity of oil. For Canada, all 10,000 oil reservoirs in western Canada were screened as to suitability for EOR on the basis of a set of criteria developed from EOR literature. Those oil reservoirs that passed were considered further in storage calculations (Shaw and Bachu, 2002).

Global estimates of storage capacity in oil reservoirs vary from 126 to 400 $GtCO_2$ (Freund, 2001). These assessments made on a top down basis include potential in undiscovered reservoirs. Comparable global capacity for CO_2 storage in gas reservoirs is estimated at 800 $GtCO_2$ (Freund, 2001). The combined estimate of total ultimate storage capacity in discovered oil and gas fields is therefore very likely to range from 675 to 900 $GtCO_2$. If undiscovered oil and gas fields are included, this figure would increase to 900 - 1,200 $GtCO_2$, but the confidence level would decrease.[1]

In comparison, more detailed regional estimates made for northwestern Europe, U.S.A., Australia, and Canada indicate a total of about 170 $GtCO_2$ storage capacity in their existing oil and gas fields, with the discovered oil and gas reserves of these countries accounting for 18.9% of the world total (USGS, 2001a). Global storage estimates based on proportionality suggest that discovered worldwide oil and gas reservoirs have a capacity of 900 $GtCO_2$, which is comparable to the global estimates by Freund (2001) of 800 $GtCO_2$ for gas (Stevens and Gale, 2000) and 123 $GtCO_2$ for oil, and is assessed to be a reliable value, although water invasion was not always taken into account.

5.3.7.2 Storage in deep saline formations

Saline formations occur in sedimentary basins throughout the world, both onshore and on the continental shelves (Chapter 2 and Section 5.3.1), and are not limited to hydrocarbon provinces or coal basins. However, estimating the CO_2 storage capacity of deep saline formations is presently a challenge because:

- There are multiple mechanisms for storage, including physical trapping beneath low permeability caprock, dissolution, and mineralization.
- These mechanisms operate both simultaneously and on different time scales, such that the time frame of CO_2 storage affects the capacity estimate; volumetric storage is important initially, but later CO_2 dissolves and reacts with minerals.
- Relations and interactions between these various mechanisms are very complex, evolve with time, and are highly dependent on local conditions.
- There is no single, consistent, broadly available methodology (various studies have used different methods that do not allow comparison).
- Only limited seismic and well data are normally available (unlike oil and gas reservoirs).

To understand the difficulties in assessing CO_2 storage capacity in deep saline formations, we need to understand the interplay of the various trapping mechanisms during the evolution of a CO_2 plume (Section 5.2 and Figure 5.18). In addition, the storage capacity of deep saline formations can only be determined on a case-by-case basis.

Figure 5.18. Schematic showing the time evolution of various CO_2 storage mechanisms operating in deep saline formations, during and following injection. Assessing storage capacity is complicated by the different time and spatial scales over which these processes occur.

To date, most of the estimates of CO_2 storage capacity in deep saline formations generally focus on physical trapping and/or dissolution. They make the simplifying assumption that no geochemical reactions take place concurrent with CO_2 injection, flow, and dissolution. Some recent work suggests that it can take several thousand years for geochemical reactions to have a significant impact (Xu et al., 2003). The CO_2 storage capacity from mineral trapping can be comparable to the capacity in solution per unit volume of sedimentary rock when formation porosity is taken into

[1] Estimates of the undiscovered oil and gas are based on the USGS assessment that 30% more oil and gas will be discovered, compared to the resources known today.

account (Bachu and Adams, 2003; Perkins et al., 2005), although the rates and time frame of these two processes are different.

Over 14 global assessments of capacity have been made using these types of approaches (GHG, 2004). The range of estimates from these studies is large (200 to 56,000 $GtCO_2$), reflecting both the different assumptions used to make these estimates and the uncertainty in the parameters. Most of the estimates are in the range of several hundred $GtCO_2$. Volumetric capacity estimates based on local, reservoir-scale numerical simulations of CO_2 injection suggest an occupancy of the pore space by CO_2 on the order of a few percent, as a result of gravity segregation and viscous fingering (van der Meer, 1992, 1995; Krom et al., 1993; Ispen and Jacobsen, 1996). Koide et al. (1992) used the areal method of projecting natural resources reserves and assumed that 1% of the total area of the world's sedimentary basins can be used for CO_2 storage. Other studies considered that 2 to 6% of formation area can be used for CO_2 storage. However, Bradshaw and Dance (2005) have shown there is no correlation between geographic area of a sedimentary basin and its capacity for either hydrocarbons (oil and gas reserves) or CO_2 storage.

The storage capacity of Europe has been estimated to be between 30 and 577 $GtCO_2$ (Holloway, 1996; Bøe et al., 2002; Wildenborg et al., 2005b). The main uncertainties for Europe are estimates of the amount trapped (estimated to be 3%) and storage efficiency, estimated to be 2–6% (2% for closed aquifer with permeability barriers; 6% for open aquifer with almost infinite extent), 4% if open/closed status not known. The volume in traps is assumed to be proportional to the total pore volume, which may not necessarily be correct. Early estimates of the total United States storage capacity in deep saline formations suggested up to 500 $GtCO_2$ (Bergman and Winter, 1995). A more recent estimate of the capacity of a single deep formation in the United States, the Mount Simon Sandstone, is 160 to 800 $GtCO_2$ (Gupta et al., 1999), suggesting that the total United States storage capacity may be higher than earlier estimates. Assuming that CO_2 will dissolve to saturation in all deep formations, Bachu and Adams (2003) estimated the storage capacity of the Alberta basin in western Canada to be approximately 4000 $GtCO_2$, which is a theoretical maximum assuming that all the pore water in the Alberta Basin could become saturated with CO_2, which is not likely. An Australian storage capacity estimate of 740 $GtCO_2$ was determined using a cumulative risked-capacity approach for 65 potentially viable sites from 48 basins (Bradshaw et al., 2003). The total capacity in Japan has been estimated to be between 1.5 and 80 $GtCO_2$, mostly in offshore formations (Tanaka et al., 1995).

Within these wide ranges, the lower figure is generally the estimated storage capacity of volumetric traps within the deep saline formations, where free-phase CO_2 would accumulate. The larger figure is based on additional storage mechanisms, mainly dissolution but also mineral trapping. The various methods and data used in these capacity estimates demonstrate a high degree of uncertainty in estimating regional or global storage capacity in deep saline formations. In the examples from Europe and Japan, the maximum estimate is between 15 and 50 times larger than the low estimate. Similarly, global estimates of storage capacity show a wide range, from 100 $GtCO_2$ to 200,000 $GtCO_2$, reflecting different methodologies, levels of uncertainties, and considerations of effective trapping mechanisms.

The assessment of this report is that it is very likely that global storage capacity in deep saline formations is at least 1,000 $GtCO_2$. Confidence in this assessment comes from the fact that oil and gas field "discovered" have a global storage capacity of approximately 675 – 900 $GtCO_2$, and that they occupy only a small fraction of the pore volume in sedimentary basins, the rest being occupied by brackish water and brine. Moreover, oil and gas reservoirs occur only in about half of the world's sedimentary basins. Additionally, regional estimates suggest that significant storage

capacity is available. Significantly more storage capacity is likely to be available in deep saline formations. The literature is not adequate to support a robust estimate of the maximum geological storage capacity. Some studies suggest that it might be little more than 1,000 $GtCO_2$ while others indicate that the upper figure could be an order of magnitude greater. More detailed regional and local capacity assessments are required to resolve this issue.

5.3.7.3 Storage in coal

No commercial CO_2-ECBM operations exist, and a comprehensive realistic assessment of the potential for CO_2 storage in coal formations has not yet been made. Normally, commercial CBM reservoirs are shallower than 1,500 m, whereas coal mining in Europe and elsewhere has reached depths of 1,000 m. Because CO_2 should not be stored in coals that could be potentially mined, there is a relatively narrow depth window for CO_2 storage.

Assuming that bituminous coals can adsorb twice as much CO_2 as methane, a preliminary analysis of the theoretical CO_2 storage potential for ECBM recovery projects suggests approximately 60 to 200 $GtCO_2$ could be stored worldwide in bituminous coal seams (IEA-GHG, 1998). More recent estimates for North America range from 60 to 90 $GtCO_2$ (Dooley et al., 2005; Reeves, 2003b), by including sub-bituminous coals and lignites. Technical and economic considerations suggest a practical storage potential of approximately 7 $GtCO_2$ for bituminous coals (Gale and Freund, 2001; Gale, 2004). Assuming that CO_2 would not be stored in coal seams without recovering the CBM, a storage capacity of 3 to 15 $GtCO_2$ is calculated, based on a U.S. annual production of CBM in 2003 of approximately 0.04 trillion m^3 and projected global production levels of 0.20 trillion m^3 in the future. This calculation assumes that 0.1 $GtCO_2$ can be stored for every Tcf of produced CBM (3.53 Gt CO_2 for every trillion m^3), and compares well to Gale (2004).

5.3.8 Matching of CO_2 sources and geological storage sites

Matching of CO_2 sources with geological storage sites requires detailed assessment of source quality and quantity, transportation, and economic and environmental factors. If the storage site is far from CO_2 sources or associated with a high level of technical uncertainty, then its storage potential may never be realized.

5.3.8.1 Regional studies

Matching sources of CO_2 to potential storage sites, taking into account projections for future socio-economic development, will be particularly important for some of the rapidly developing economies. Assessment of sources and storage sites, together with numerical simulations, emissions mapping, and identification of transport routes, has been undertaken for a number of regions in Europe (Holloway, 1996; Larsen et al., 2005). In Japan, studies have modeled and optimized the linkages between 20 onshore emission regions and 20 offshore storage regions, including both ocean storage and geological storage (Akimoto et al., 2003). Preliminary studies have also begun in India (Garg et al., 2005) and Argentina (Amadeo et al., 2005). For the United States, a study using a Geographic Information System (GIS) and a broad-based economic analysis (Dooley et al., 2005) shows that about two-thirds of power stations are adjacent to potential geological storage locations, but a number would require transportation of hundreds of kilometers.

Studies of Canadian sedimentary basins that include descriptions of the type of data and flow diagrams of the assessment process have been carried out by Bachu (2003). Results for the Western Canada Sedimentary Basin show that, while the total capacity of oil and gas reservoirs in the basin is several $GtCO_2$, the capacity of underlying deep saline formations is two to three orders of

magnitude higher. Most major CO_2 emitters have potential storage sites in relative close proximity, with the notable exception of the oil sands plants in northeastern Alberta (current CO_2 emissions of ~20 $MtCO_2$ per year).

In Australia, a portfolio approach was undertaken for the continent to identify a range of geological storage sites (Rigg et al., 2001; Bradshaw et al., 2002). The initial assessment screened 300 sedimentary basins down to 48 basins and 65 areas. Methodology was developed for ranking of sites (technical and economic risks) and consideration of large CO_2 emission sites to assess storage sites. Region-wide solutions were sought, incorporating an economic model to assess full project economics over 20 to 30 years, including costs of transportation, storage, monitoring, and Monte Carlo analysis. The study produced three storage estimates:

- Total capacity of 740 $GtCO_2$, equivalent to 1,600 years of current emissions, but with no economic barriers considered.
- "Realistic" capacity of 100 to 115 $MtCO_2$ per annum or 50% of annual stationary emissions, determined by matching sources with the closest viable storage sites and assuming economic incentives for storage.
- "Cost curve" capacity of 20 to 180 $MtCO_2$ per annum, with increasing storage capacity depending on future CO_2 values.

5.3.8.2 Methodology and assessment criteria

Although some commonality exists in the various approaches for capacity assessment, each study is influenced by the available data and resources, the aims of the respective study, and whether local or whole-region solutions are being sought. The next level of analysis covers regional aspects and detail at the prospect/project level, including screening and selection of potential CO_2 storage sites on the basis of technical, environmental, safety, and economic criteria. Finally, integration and analysis of various scenarios can lead to identification of potential storage sites that should then become targets of detailed engineering and economic studies.

During selection of CO_2 storage sites and matching them with CO_2 sources, the following should be considered (Winter and Bergman, 1993; Bergman et al., 1997; Kovscek, 2002): volume, purity and rate of the CO_2 stream; suitability of the storage sites, including the seal; proximity of the source and storage sites; infrastructure for the capture and delivery of CO_2; existence of a large number of storage sites to allow diversification; known or undiscovered energy, mineral, or groundwater resources that might be compromised; existing wells and infrastructure; viability and safety of the storage site; injection strategies and, in the case of EOR and ECBM, production strategies, which together affect the number of wells and their spacing; terrain and right of way; location of population centers; local expertise; and overall costs and economics.

Although technical suitability criteria are initial indicators for identifying potential CO_2 storage sites, once the best candidates have been selected, further considerations will be controlled by economic, safety, and environmental aspects. These criteria must be assessed for the anticipated lifetime of the operation, to ascertain whether storage capacity can match supply volume and whether injection rates can match the supply rate. Other issues might include whether CO_2 sources and storage sites are matched on a one-to-one basis, or whether a collection and distribution system is implemented, to form an integrated industrial system. Such deliberations affect cost outcomes, as will the supply rates, through economies of scale. Early opportunities for source-storage matching could involve sites where an economic benefit might accrue through the enhanced production of oil or gas (Holtz et al., 2001; van Bergen et al., 2003b).

Assigning technical risks is important for matching of CO_2 sources and storage sites, based on five risk factors: storage capacity, injectivity, containment, site, and natural resources (Bradshaw et al., 2002, 2003). These screening criteria introduce reality checks to large storage-capacity estimates and indicate which regions to concentrate upon in future detailed studies. The use of "cost curve capacity" introduces another level of sophistication that helps in identifying how sensitive any storage capacity estimate is to the cost of CO_2. Combining the technical criteria into an economic assessment reveals that costs are quite project-specific.

5.4 Characterization and Performance Prediction for Identified Sites

Key goals for geological CO_2 storage site characterization are to assess how much CO_2 can be stored at a potential storage site, and to demonstrate that the site is capable of meeting required storage performance criteria (Figure 5.19). Site characterization requires the collection of the wide variety of geological data that are needed to achieve these goals. Much of the data will necessarily be site specific. Most data will be integrated into geological models that will be used to simulate and predict the performance of the site. These and related issues are considered below.

Figure 5.19. Life cycle of a CO_2 storage project showing the importance of integrating site characterisation with a range of regulatory, monitoring, economic, risking and engineering issues.

5.4.1 Characterization of Identified Sites

Storage site requirements depend greatly upon the trapping mechanism and the geological medium in which storage is proposed (e.g. deep saline formation, depleted oil or gas field, or coal seam). Data availability and quality vary greatly between each of these options (Table 5.3). In many cases, oil and gas fields will be better characterized than deep saline formations because a relevant data set was collected during hydrocarbon exploration and production. However, this may not always be the case. There are many examples of deep saline formations whose character and performance for CO_2 storage can be predicted reliably over a large area (Chadwick et al., 2003; Bradshaw et al., 2003).

5.4.1.1 Data Types

The storage site and its surroundings need to be characterized in terms of geology, hydrogeology, geochemistry, and geomechanics (structural geology and deformation in response to stress changes). The greatest emphasis will be placed on the reservoir and its sealing horizons. However, the strata above the storage formation and caprock also need to be assessed, because if CO_2 leaked it would migrate through them (Haidl et al., 2005). Documentation of the characteristics of any particular storage site will rely on data that have been obtained directly from the reservoir, such as core and fluids produced from wells at or near the proposed storage site, pressure transient tests conducted to test seal efficiency, and indirect remote sensing measurements, such as seismic reflection data, and regional hydrodynamic pressure gradients. Integration of all of the different types of data is needed to develop a reliable model that can be used to assess whether a site is suitable for CO_2 storage.

During the site-selection process that may follow an initial screening, detailed reservoir simulation (Section 5.4.4) will be necessary to meaningfully assess a potential storage site. A range of geophysical, geological, hydrogeological, and geomechanical information is required to perform the modeling associated with a reservoir simulation. This information must be built into a three-dimensional geological model, populated with known and extrapolated data at an appropriate scale. Examples of the basic types of data and products that may be useful are listed in Table 5.3.

Table 5.3. Types of data that are used to characterize and select geological storage sites.

Financial constraints may limit the types of data that can be collected as part of the site characterization and selection process. Today, there is no standard methodology that prescribes how a site must be characterized. Instead, selections about site characterization data will be made on a site-specific basis, choosing those data sets that will be most valuable in the particular geological setting. However, there are some data sets that are likely to be selected for every case. Geological site description from wellbores and outcrops are needed to characterize the storage formation and seal properties. Seismic surveys are needed to define the subsurface geological structure and identify faults or fractures that could create leakage pathways. Formation pressure measurements are needed to map the rate and direction of groundwater flow. Water quality samples are needed to demonstrate the isolation between deep and shallow groundwater.

5.4.1.2 Assessment of stratigraphic factors affecting site integrity

Caprocks or seals are the permeability barriers (mostly vertical but sometimes lateral) that prevent or impede migration of CO_2 from the injection site. The integrity of a seal depends on spatial distribution and physical properties. Ideally, a sealing rock unit should be regional in nature and uniform in lithology, especially at its base. Where there are lateral changes in the basal units of a seal rock, the chance of migration out of the primary reservoir into higher intervals increases. However, if the seal rock is uniform, regionally extensive, and thick, then the main issues will be the physical rock strength, any natural or man-made penetrations (faults, fractures and wells) and potential CO_2-water-rock reactions that could weaken the seal rock or increase its porosity and permeability.

Methods have been described for making field-scale measurements of the permeability of caprocks for formation gas storage projects, based on theoretical developments in the 1950s and 1960s (Hantush and Jacobs, 1955; Hantush, 1960). These use water-pumping tests to measure the rate of leakage across the caprock (Witherspoon et al., 1968). A related type of test, called a pressure "leak-off" test, can be used to measure caprock permeability and *in situ* stress. The capacity of a seal rock to hold back fluids can also be estimated from core samples using mercury injection capillary pressure (MICP) analysis, a method widely used in the oil and gas industry (Vavra et al., 1992). MICP analysis measures the pressures required to move mercury through the pore network system of a seal rock. The resulting data can be used to derive the height of a column of reservoir rock saturated by a particular fluid (e.g., CO_2) that the sealing strata would be capable of holding back (Gibson-Poole et al., 2002).

5.4.1.3 Geomechanical factors affecting site integrity

When CO_2 is injected into a porous and permeable reservoir rock, it will be forced into pores at a pressure higher than that in the surrounding formation. This pressure could lead to deformation of the reservoir rock or the seal rock, resulting in the opening of fractures or failure along a fault plane. Geomechanical modeling of the subsurface is necessary in any storage site assessment and should focus on the maximum formation pressures that can be sustained in a storage site. As an example, at Weyburn, where the initial reservoir pressure is 14.2 MPa, the maximum injection pressure (90% of fracture pressure) is in the range of 25-27 MPa, and fracture pressure is in the range of 29-31 MPa. Coupled geomechanical/geochemical modeling may also be needed to document fracture sealing by precipitation of carbonates in fractures or pores. Modeling these will require knowledge of pore fluid composition, mineralogy, *in situ* stresses, pore fluid pressures, and pre-existing fault orientations and their frictional properties (Johnson et al., 2005; Streit and Hillis,

2003). These estimates can be made using conventional well and seismic data and leak-off tests, but the results can be enhanced by access to physical measurements of rock strength. Application of this methodology at a regional scale is documented by Gibson-Poole et al. (2002).

The efficacy of an oil or gas field seal rock can be characterized by examining its capillary entry pressure and the potential hydrocarbon column height that it can sustain (see above). However, Jimenez and Chalaturnyk (2003) suggest that the geomechanical processes, during depletion and subsequent CO_2 injection, may affect the hydraulic integrity of the seal rock in hydrocarbon fields. Movement along faults can be produced in a hydrocarbon field by induced changes in the pre-production stress regime. This can happen when fluid pressures are substantially depleted during hydrocarbon production (Streit and Hillis, 2003). Determining whether the induced stress changes result in compaction or pore collapse is critical in assessment of a depleted field. If pore collapse occurs, then it might not be possible to return a pressure-depleted field to its original pore pressure without the risk of induced failure. By having a reduced maximum pore fluid pressure, the total volume of CO_2 that can be stored in a depleted field could be substantially less than otherwise estimated.

5.4.1.4 Geochemical factors affecting site integrity

The mixing of CO_2 and water in the pore system of the reservoir rock will create dissolved CO_2, carbonic acid, and bicarbonate ions. The acidification of the pore water reduces the amount of CO_2 that can be dissolved. As a consequence, rocks that buffer the pore water pH to higher values (reducing the acidity) facilitate the storage of CO_2 as a dissolved phase (Section 5.2). The CO_2-rich water may react with minerals in the reservoir rock or caprock matrix, or with the primary pore fluid. Importantly, it may also react with borehole cements and steels (see discussion below). Such reactions may cause either mineral dissolution and potential breakdown of the rock (or cement) matrix, or mineral precipitation and plugging of the pore system (and thus, reduction in permeability).

A carbonate mineral formation effectively traps stored CO_2 as an immobile solid phase (Section 5.2). If the mineralogical composition of the rock matrix is strongly dominated by quartz, geochemical reactions will be dominated by simple dissolution into the brine, and CO_2-water-rock reactions can be neglected. In this case, complex geochemical simulations of rock-water interactions will not be needed. However, for more complex mineralogies, sophisticated simulations, based on laboratory experimental data using reservoir and caprock samples and native pore fluids, may be necessary to fully assess the potential effects of such reactions in more complex systems (Bachu et al., 1994; Czernichowski-Lauriol et al., 1996; Gunter et al., 2000; Rochelle et al., 1999, 2004). Studies of rock samples recovered from natural systems rich in CO_2 can provide indications of what reactions might occur in the very long term (Pearce et al., 1996). Reactions in boreholes are considered by Crolet (1983), Rochelle et al. (2004) and Schremp and Roberson (1975). Natural CO_2 reservoirs also allow sampling of solid and fluid reactants and reaction products, thus allowing formulation of geochemical models that can be verified with numerical simulations, further facilitating quantitative predictions of water-CO_2-rock reactions (May, 1998).

5.4.1.5 Man-made factors affecting storage integrity

As discussed at greater length in Section 5.7.2, man-made factors such as active or abandoned wells, mine shafts, and subsurface production can impact storage security. Abandoned wells that penetrate the storage formation can be of particular concern, because they may provide short circuits for CO_2 to leak from the storage formation to the surface (Celia and Bachu, 2003; Gasda et al., 2004). Therefore, locating and assessing the condition of abandoned and active wells is an

important component of site characterization. It is possible to locate abandoned wells using airborne magnetometer surveys. In the majority of cases, abandoned wells will have metal casings, but this may not be the case for wells drilled long ago, or those never completed for oil or gas production. Countries with oil and gas production will have at least some records of the more recently drilled wells, depth of wells, and other information stored in a geographic database. The consistency and quality of record keeping of drilled wells (oil and gas, mining exploration, and water) varies considerably, from excellent for recent wells to nonexistent, particularly for older wells (Stenhouse et al., 2004).

5.4.2 Performance prediction and optimization modeling

Computer simulation also has a key role in the design and operation of field projects for underground injection of CO_2. Predictions of the storage capacity of the site, or the expected incremental recovery in enhanced recovery projects, are vital to an initial assessment of economic feasibility. In a similar vein, simulation can be used in tandem with economic assessments to optimize the location, number, and design, and depth of injection wells. For enhanced recovery projects, the timing of CO_2 injection relative to production is vital to the success of the operation, and the effect of various strategies can be assessed by simulation. Simulations of the long-term distribution of CO_2 in the subsurface (e.g., migration rate and direction, and rate of dissolution in the formation water) are important for the design of cost-effective monitoring programs, since the results will influence the location of monitoring wells and the frequency of repeat measurements, such as for seismic, soil gas, or water chemistry. During injection and monitoring operations, simulation models can be adjusted to match field observations and then used to assess the impact of possible operational changes, such as drilling new wells or altering injection rates, often with the goal of further improving recovery (in the context of hydrocarbon extraction) or of avoiding migration of CO_2 passed a likely spill-point.

Section 5.2 described the important physical, chemical, and geomechanical processes that must be considered when evaluating a storage project. Numerical simulators currently in use in the oil, gas, and geothermal energy industries provide important subsets of the required capabilities. They have served as convenient starting points for recent and ongoing development efforts specifically targeted at modeling the geological storage of CO_2. Many simulation codes have been used and adapted for this purpose (Nitao, 1996; Pruess et al., 1999; White and Oostrom, 1997; Steefel, 2001; White, 1995; Lichtner, 2001; Xu et al., 2003).

Simulation codes are available for multiphase flow processes, chemical reactions, and geomechanical changes, but most codes account for only a subset of these processes. Capabilities for a comprehensive treatment of different processes are limited at present. This is especially true for the coupling of multiphase fluid flow, geochemical reactions, and (particularly) geomechanics, which are very important for the integrity of potential geological storage sites (Rutqvist and Tsang, 2002). Demonstrating that they can model the important physical and chemical processes accurately and reliably is necessary for establishing credibility as practical engineering tools. Recently, an analytical model developed for predicting the evolution of a plume of CO_2 injected into a deep saline formation, as well as potential CO_2 leakage rates through abandoned wells, has shown good matching with results obtained using the industry numerical simulator ECLIPSE (Celia et al., 2005; Nordbotten et al., 2005b).

A code intercomparison study involving ten research groups from six countries was conducted recently to evaluate the capabilities and accuracy of numerical simulators for geological storage of greenhouse gases (Pruess et al., 2004). The test problems addressed CO_2 storage in saline

formations and oil and gas reservoirs. The results of the intercomparison were encouraging, in that substantial agreement was found between results obtained with different simulators. However, there were also areas with only fair agreement, as well as some significant discrepancies. Most discrepancies could be traced to differences in fluid property descriptions, such as fluid densities and viscosities, and mutual solubility of CO_2 and water. The study concluded that "although code development work undoubtedly must continue . . . codes are available now that can model the complex phenomena accompanying geological storage of CO_2 in a robust manner and with quantitatively similar results" (Pruess et al., 2004).

Another, similar intercomparison study was conducted for simulation of storage of CO_2 in coal beds, considering both pure CO_2 injection and injection of flue gases (Law et al., 2003). Again, there was good agreement between the simulation results from different codes. Code intercomparisons are useful for checking mathematical methods and numerical approximations, and to provide insight into relevant phenomena using the different descriptions of the physics (or chemistry) implemented. However, establishing the realism and accuracy of physical and chemical process models is a more demanding task, one that requires carefully controlled and monitored field and laboratory experiments. Only after simulation models have been shown to be capable of adequately representing real-world observations can they be relied upon for engineering design and analysis. Methods for calibrating models to complex engineered subsurface systems are available, but validating them requires field testing that is time consuming and expensive.

The principal difficulty is that the complex geological models on which the simulation models are based are subject to considerable uncertainties, resulting both from uncertainties in data interpretation and, in some cases, sparse data sets. Measurements taken at wells provide information on rock and fluid properties at that location, but statistical techniques must be used to estimate properties away from the wells. When simulating a field in which injection or production is already occurring, a standard approach in the oil and gas industry is to adjust some parameters of the geological model to match selected field observations. This does not prove that the model is correct, but it does provide additional constraints on the model parameters. In the case of saline formation storage, history matching is generally not feasible for constraining uncertainties, due to a lack of underground data for comparison. Systematic parameter variation routines and statistical functions should be included in future coupled simulators to allow uncertainty estimates for numerical reservoir simulation results.

Field tests of CO_2 injection are are under way or planned in several countries, and these tests provide opportunities to validate simulation models. For example, in Statoil's Sleipner project, simulation results have been matched to information on the distribution of CO_2 in the subsurface, based on the interpretation of repeat 3D seismic surveys (Lindeberg et al., 2001; van der Meer et al., 2001; see also Section 5.4.4). At the Weyburn project in Canada, repeat seismic surveys and water chemistry sampling provide information on CO_2 distribution that can likewise be used to adjust the simulation models (Moberg et al., 2003; White et al., 2004).

Predictions of the long-term distribution of injected CO_2, including the effects of geochemical reactions, cannot be directly validated on a field scale because these reactions may take hundreds to thousands of years. However, the simulation of important mechanisms, such as the convective mixing of dissolved CO_2, can be tested by comparison to laboratory analogues (Ennis-King and Paterson, 2003). Another possible route is to match simulations to the geochemical changes that have occurred in appropriate natural underground accumulations of CO_2, such as the precipatation of carbonate minerals, since these provide evidence for the slow processes that affect the long-term distribution of CO_2 (Johnson et al., 2005). It is also important to have reliable and accurate data

regarding the thermophysical properties of CO_2 and mixtures of CO_2 with methane, water, and potential contaminants such as H_2S and SO_2. Similarly, it is important to have data on relative permeability and capillary pressure under drainage and imbibition conditions. Code comparison studies show that the largest discrepancies between different simulators can be traced to uncertainties in these parameters (Pruess et al., 2004). For sites where few, if any, CO_2-water-rock interactions occur, reactive chemical transport modeling may not be needed, and simpler simulations that only consider CO_2-water reactions will suffice.

5.4.3 Examples of storage site characterization and performance prediction

Following are examples and lessons learned from two case studies of characterization of a CO_2 storage site: one of an actual operating CO_2 storage site (Sleipner Gas Field in the North Sea) and the other a potential or theoretical site (Petrel Sub-basin offshore northwest Australia). A common theme throughout these studies is the integration and multidisciplinary approach required to adequately document and monitor any injection site. There are lessons to be learned from these studies, because they have identified issues that in hindsight should be examined prior to any CO_2 injection.

5.4.3.1 Sleipner

Studies of the Sleipner CO_2 Injection Project (Section 5.2) highlighted the advantages of detailed knowledge of the reservoir stratigraphy (Chadwick et al., 2003). After the initial CO_2 injection, small layers of low permeability sediments within the saline formation interval and sandy lenses near the base of the seal were clearly seen to be exercising an important control on the distribution of CO_2 within the reservoir rock (Figure 5.16a,b). Time-lapse three-dimensional seismic imaging of the developing CO_2 plume also identified the need for precision depth mapping of the bottom of the caprock interval. At Sleipner, the top of the reservoir is almost flat at a regional scale. Hence, any subtle variance in the actual versus predicted depth could substantially affect migration patterns and rate. Identification and mapping of a sand lens above what was initially interpreted as the top of the reservoir resulted in a significant change to the predicted migration direction of the CO_2 (Figure 5.16a,b). These results show the benefit of repeated 3D seismic monitoring and integration of monitoring results into modeling during the injection phase of the project; and that refinement of storage-site characterization continues after injection has started.

5.4.3.2 Petrel Sub-basin

A theoretical case study of the Petrel Sub-basin offshore northwest Australia examined the basin-wide storage potential of a combined hydrodynamic and solution trapping mechanism, and identified how sensitive a reservoir simulation will be to the collected data and models built during the characterization of a storage site (Gibson-Poole et al., 2002; Ennis-King et al., 2003). As at Sleipner, the Petrel study identified that vertical permeability and shale beds within the reservoir interval of the geological model strongly influenced the vertical CO_2 migration rate. In the reservoir simulation, using coarser grids overestimated the dissolution rate of CO_2 during the injection period, but underestimated it during the long-term migration period. Lower values of residual CO_2 saturation lead to faster dissolution during the long-term migration period, and the rate of complete dissolution depended on the vertical permeability. Migration distance depended on the rate of dissolution and residual CO_2 trapping. The conclusion of the characterization and performance prediction studies is that the Petrel Sub-basin has a regionally extensive reservoir/seal pair suitable for hydrodynamic trapping (Section 5.2). While the characterization was performed using only a few wells with limited data, analogue studies helped define the characteristics of the formation.

Although this is not the ideal situation, performing a reservoir simulation using geological analogues may often be the only option. However, understanding which elements will be the most sensitive in the simulation will help geoscientists to understand where to prioritize their efforts in data collection and interpretation.

5.5 Injection Well Technology and Field Operations

So far in this chapter, we have only considered the nature of the storage site. But once a suitable site is identified, do we have the technology available to inject large quantities of CO_2 (~1 to 10 $MtCO_2$/yr) into the subsurface and to operate the site effectively and safely? This section examines the issue of technology availability.

5.5.1 Injection well technologies

As pointed out earlier in this chapter, many of the technologies required for large-scale geological storage of CO_2 already exist. Drilling and completion technology for injection wells in the oil and gas industry has evolved to a highly sophisticated state, such that it is now possible to drill and complete vertical and extended reach wells (including horizontal wells) in deep formations, wells with multiple completions, and wells able to handle corrosive fluids. Based on extensive oil industry experience, the technologies for drilling, injection, stimulations, and completions for CO_2 injection wells exist and are being practiced with some adaptations in current CO_2 storage projects. In a CO_2 injection well, the principal well design considerations include pressure, corrosion-resistant materials, and production and injection rates.

The design of a CO_2 injection well is very similar to that of a gas injection well in an oil field or natural gas storage project. Most downhole components need to be upgraded for higher pressure ratings and corrosion resistance. The technology for handling CO_2 has already been developed for EOR operations and for the disposal of acid gas (Section 5.2.3). Horizontal and extended reach wells can be good options for improving the rate of CO_2 injection from individual wells. The Weyburn field in Canada (Box 5.3) is an example in which the use of horizontal injection wells is improving oil recovery and increasing CO_2 storage. The horizontal injectors reduce the number of injection wells required for field development. A horizontal injection well has the added advantage that it can create injection profiles that reduce the adverse effects of injected-gas preferential flow through high-permeability zones.

Figure 5.20. Typical CO_2 injection well and wellhead configuration.

The number of wells required for a storage project will depend on a number of factors, including total injection rate, permeability and thickness of the formation, maximum injection pressures, and availability of land surface area for the injection wells. In general, fewer wells will be needed for high-permeability sediments in thick storage formations and for those projects with horizontal wells for injection. For example, the Sleipner Project, which injects CO_2 into a high-permeability, 200-m thick formation uses only one well to inject 1 $MtCO_2$ per year (Korbol and Kaddour, 1994). In contrast, at the In Salah Project in Algeria, CO_2 is injected into a 20 m thick formation with much lower permeability (Riddiford et al., 2003). Here, three long-reach horizontal wells with slotted intervals over 1 km are used to inject 1 $MtCO_2$ per year (Figure 5.5). Cost will depend, to some degree, on the number and completion techniques for these wells. Therefore, careful design and optimization of the number and slotted intervals is important for cost-effective storage projects.

An injection well and a wellhead are depicted in Figure 5.20. Injection wells commonly are equipped with two valves for well control, one for regular use and one reserved for safety shutoff. In acid gas injection wells, a downhole safety valve is incorporated in the tubing, so that if equipment fails at the surface, the well is automatically shut down to prevent back flow. Jarrell et al. (2002) recommend an automatic shutoff valve on all CO_2 wells to ensure that no release occurs and to prevent CO_2 from inadvertently flowing back into the injection system. A typical downhole configuration for an injection well includes a double-grip packer, an on-off tool, and a downhole shutoff valve. Annular pressure monitors help detect leaks in packers and tubing, which is important for taking rapid corrective action. To prevent dangerous high-pressure buildup on surface equipment and avoid CO_2 releases into the atmosphere, CO_2 injection must be stopped as soon as leaks occur. Rupture disks and safety valves can be used to relieve built-up pressure. Adequate plans need to be in place for dealing with excess CO_2 if the injection well needs to be shut in. Options include having a backup injection well or methods to safely vent CO_2 to the atmosphere.

Proper maintenance of CO_2 injection wells is necessary to avoid leakage and well failures. Several practical procedures can be used to reduce probabilities of CO_2 blow-out (uncontrolled flow) and mitigate the adverse effects if one should occur. These include: periodic wellbore integrity surveys on drilled injection wells, improved blow-out prevention (BOP) maintenance, installation of additional BOP on suspect wells, improved crew awareness, contingency planning, and emergency response training (Skinner, 2003).

For CO_2 injection through existing and old wells, key factors include the mechanical condition of the well and quality of the cement and well maintenance. A leaking wellbore annulus can be a pathway for CO_2 migration. Detailed logging programs for checking wellbore integrity can be conducted by the operator to protect formations and prevent reservoir cross-flow. A well used for injection (Figure 5.20) must be equipped with a packer to isolate pressure to the injection interval. All materials used in injection wells should be designed to anticipate peak volume, pressure, and temperature. In the case of wet gas (containing free water), use of corrosion-resistant material is essential.

5.5.2 Well abandonment procedures

Abandonment procedures for oil, gas, and injection wells are designed to protect drinking water aquifers from contamination. If a well remains open after it is no longer in use, it is possible that brines, hydrocarbons, or CO_2 could migrate up the well and into shallow drinking water aquifers. To avoid this, many countries have developed regulations for well "abandonment" or "closure" (for example, United States Code of Federal Regulations 40 Part 144, and EUB, 2003). These procedures usually require placing cement or mechanical plugs in all or part of the well. Extra care is usually taken to seal the well adjacent to drinking water aquifers. Examples of well abandonment procedures for cased and uncased wells are shown in Figure 5.21. Tests are often required to locate the depth of the plugs and test their mechanical strength under pressure.

Figure 5.21. Examples of how cased and uncased wells are abandoned today. Special requirements may be developed for abandoning CO_2 storage wells, including use of corrosion resistant cement plugs and removing all or part of the casing in the injection interval and caprock.

It is expected that abandonment procedures for CO_2 wells could broadly follow the abandonment methodology used for oil and gas wells and acid-gas disposal wells. However, special care has to be taken to use sealing plugs and cement that are resistant to degradation from CO_2. Carbon dioxide-resistant cements have been developed for oil field and geothermal applications. It has been

suggested that removing the casing and the liner penetrating the caprock could avoid corrosion of the steel that may later create channels for leakage. The production casing can be removed by pulling or drilling (milling) it out. After removing the casing, a cement plug can be put into the open borehole, as illustrated in Figure 5.21.

The cement plug will act as the main barrier to future CO_2 migration. A major issue is related to the sealing quality of the cement plug and the bonding quality with the penetrated caprock. Microchannels created near the wellbore during drilling or milling operations should be sealed with cement. Fluid could also possibly be flushed into the storage reservoir to displace the CO_2 and help to improve the cementing quality and bonding to the sealing caprock. Casing protective materials and alternative casing materials, for example composites, should also be evaluated for possible and alternative abandonment procedures. Sealing performance of abandoned wells may need to be monitored for some time after storage operations are completed.

5.5.3 Injection well pressure and reservoir constraints

Injectivity characterizes the ease with which fluid can be injected into a geological formation and is defined as injection rate, divided by the pressure difference between the injection point inside the well and the formation. Although CO_2 injectivity should be significantly greater than brine injectivity (because CO_2 has a much lower viscosity than brine), this is not always the case. Grigg (2005) analyzed the performance of CO_2 floods in west Texas and concluded that, in more than half of the projects, injectivity was lower than expected or decreased over time. Christman and Gorell (1990) showed that unexpected CO_2-injectivity behavior in EOR operations is caused primarily by differences in flow geometry and fluid properties of the oil. Injectivity changes can also be related to insufficiently known relative-permeability effects.

To introduce CO_2 into the storage formation, the downhole injection pressure must be higher than the reservoir fluid pressure. On the other hand, increasing formation pressure may induce fractures in the formation. Regulatory agencies normally limit the maximum downhole pressure to avoid fracturing the injection formation. Measurement of *in situ* formation stresses and pore fluid pressure are needed for establishing safe injection pressures. Depletion of fluid pressure during production can affect the state of stress in the reservoir. Analysis of some depleted reservoirs indicated that horizontal rock stress decreased by 50% to 80% of the pore pressure decrease, which increased the possibility of fracturing the reservoir (Streit and Hillis, 2003).

Safe injection pressures can vary widely, based on the state of stress and tectonic history of a basin. Regulatory agencies have determined safe injection pressures based on experience in specific oil and gas provinces. Van der Meer (1996) has derived a relationship for the maximum safe injection pressure. This relationship indicated that for a depth down to 1,000 m, the maximum injection pressure is estimated to be 1.35 times the hydrostatic pressure - and this increased to 2.4 for depths ranging from 1 to 5 km. The maximum pressure gradient allowed for natural gas stored in an aquifer in Germany is 16.8 kPa/m (Sedlacek, 1999). This value exceeds the natural pressure gradients of formation waters in northeastern Germany, which are on the order of 10.5 to 13.1 kPa/m. In Denmark or Great Britain, the maximum pressure gradients for aquifer storage of natural gas do not exceed hydrostatic gradients. In the U.S.A., for industrial waste-water injection wells, injection pressure must not exceed fracture initiation or propagation pressures in the injection formation (USEPA, 1994). For oil and gas field injection wells, injection pressures must not exceed those that would initiate or propagate fractures in the confining units. In the U.S.A., States are delegated authority to establish maximum injection pressures. Until the 1990s, many states set state-wide standards for maximum injection pressures. Values ranged from 13 kPa/m to18 kPa/m. More recently, regulations have changed to require site-specific tests to establish maximum

injection pressure gradients. Practical experience in the USEPA's Underground Injection Control Program has shown fracture pressures to range between 11 and 21 kPa/m.

5.5.4 Field operations and surface facilities

A comparison of injection rates for selected current CO_2 storage projects in enhanced oil recovery and acid gas injection is shown in Figure 5.23. As indicated, the amount of CO_2 injected from a 500 MW coal-fired power plant would fall within the range of existing experience of CO_2 injection operations for EOR. These examples therefore offer a great deal of insight as to how a geological storage regime might evolve, operate, and be managed safely and effectively.

CO_2-EOR operations fall into one of three groups (Jarrell et al., 2002):
Reservoir management - what to inject, how fast to inject, how much to inject, how to manage water-alternating-gas (WAG), how to maximize sweep efficiency, etc.
Well management - producing method and remedial work, including selection of workovers, chemical treatment, and CO_2 breakthrough.
Facility management - reinjection plant, separation, metering, corrosion control, and facility organization.

Typically, CO_2 is transported from its source to an EOR site through a pipeline and is then injected into the reservoir through an injection well, usually after compression. Before entering the compressor, a suction scrubber will remove any residual liquids present in the CO_2 stream. In EOR operations, CO_2 produced from the production well along with oil and water is separated and then injected back through the injection well.

The field application of CO_2-ECBM technology is broadly similar to that of EOR operations. Carbon dioxide is transported to the CBM field and injected in the coal seam through dedicated injection wells. At the production well, coal-seam gas and formation water is lifted to the surface using electric pumps.

According to Jarrell et al. (2002), surface facilities for CO_2-EOR projects include:

- Production systems-fluid separation, gas gathering, production satellite, liquid gathering, central battery, field compression, and emergency shutdown systems
- Injection systems-gas repressurization, water injection, and CO_2 distribution systems
- Gas processing systems-gas processing plant, H_2S removal systems, and sulphur recovery and disposal systems.

Jarrell et al. (2002) point out that CO_2 facilities are similar to those used in conventional facilities such as for waterfloods. Differences result from the effects of multiphase flow, selection of different materials, and the higher pressure that must be handled. The CO_2 field operation set up for the Weyburn Field is shown in Figure 5.22.

Figure 5.22. Typical CO_2 field operation set up: Weyburn surface facilities.

It is common to use existing facilities for new CO_2 projects to reduce capital costs, although physical restrictions are always present. Starting a CO_2 flood in an old oil field can affect almost every process and facility (Jarrell et al., 2002); for example, (1) the presence of CO_2 makes the produced water much more corrosive; (2) makeup water from new sources may interact with formation water to create new problems with scale or corrosion; (3) a CO_2 flood may cause paraffins and asphaltenes to precipitate out of the oil, which can cause plugging and emulsion

problems; and (4) the potentially dramatic increase in production caused by the flood could cause more formation fines to be entrained in the oil, potentially causing plugging, erosion, and processing problems.

Figure 5.23. Comparison of the magnitude of CO_2 injection activities illustrating that the storage operations from a typical 500 MW coal plant will be on the same order of magnitude as existing CO_2 injection operations (after Heinrich et al., 2003).

5.6 Monitoring and Verification Technology

What actually happens to CO_2 in the subsurface and how do we know what is happening? In other words, can we monitor CO_2 once it is injected? What techniques are available for monitoring whether CO_2 is leaking out of the storage formation, and how sensitive are they? Can we verify that CO_2 is safely and effectively stored underground? How long is monitoring needed? These are the questions that are addressed in this section of the report.

5.6.1 Purposes for monitoring

Monitoring is needed for a wide variety of purposes. Specifically, monitoring can be used to:

- Ensure and document effective injection well controls, specifically for monitoring the condition of the injection well and measuring injection rates, wellhead, and formation pressures. Petroleum industry experience suggests that leakage from the injection well itself, resulting from improper completion or deterioration of the casing, packers, or cement, is one of the most significant potential failure modes for injection projects (Perry, 2005; Apps, 2005).
- Verify the quantity of injected CO_2 that has been stored by various mechanisms.
- Optimize the efficiency of the storage project, including utilization of the storage volume, injection pressures and drilling of new injection wells.
- Demonstrate with appropriate monitoring techniques that CO_2 remains contained in the intended storage formations(s). This is currently the principal method for assuring that the CO_2 remains stored and that performance predictions can be verified.
- Detect leakage and provide an early warning of any seepage or leakage that might require mitigating action.

In addition to essential elements of a monitoring strategy, there are other parameters that can be used to optimize storage projects, deal with unintended leakage, and address regulatory, legal, and social issues. Other important purposes include assessing the integrity of plugged or abandoned wells, calibrating and confirming performance assessment models (including "history matching"), establishing baseline parameters for the storage site to ensure that CO_2-induced changes are recognized (Wilson and Monea, 2005), detecting microseismicity associated with a storage project, measuring surface fluxes of CO_2, and designing and monitoring remediation activities (Benson et al., 2004).

Before monitoring of subsurface storage can take place effectively, a baseline survey must be taken. This survey provides the point of comparison for subsequent surveys. This is particularly true of seismic and other remote-sensing technologies, where the identification of saturation of fluids with CO_2 is based on comparative analysis. Baseline monitoring is also a prerequisite for geochemical monitoring, where anomalies are identified relative to background concentrations. Additionally, establishing a baseline of CO_2 fluxes resulting from ecosystem cycling of CO_2, both on diurnal and annual cycles, are useful for distinguishing natural fluxes from potential storage-related releases.

Much of the monitoring technology described below was developed for application in the oil and gas industry. The majority of these techniques can be applied to monitoring storage projects in all types of geological formations, although there remains much to be learned about monitoring coal formations. Monitoring experience from natural gas storage in saline aquifers can also provide a useful industrial analogue.

5.6.2 Technologies for monitoring injection rates and pressures

Measurements of CO_2 injection rates are a common oil field practice, and instruments for this purpose are available commercially. Measurements are made using gauges either at the injection wellhead or near distribution manifolds. Typical systems use orifice meters or other devices that relate the pressure drop across the device to the flow rate. The accuracy of the measurements depends on a number of factors that have been described in general by Morrow et al. (2003) and specifically for CO_2 by Wright and Majek (1998). For CO_2, accurate estimation of the density is most important for improving measurement accuracy. Small changes in temperature, pressure, and composition can have large effects on density. Wright and Majek (1998) developed an oil field CO_2 flow rate system by combining pressure, temperature, and differential pressure measurements with gas chromatography. The improved system had an accuracy of 0.6%, compared to 8% for the conventional system. Standards for measurement accuracy vary and are usually established by governments or industrial associations. For example, in the U.S.A., current auditing practices for CO_2 EOR accept flow meter precision of plus or minus 4%.

Measurements of injection pressure at the surface and in the formation are also routine. Pressure gauges are installed on most injection wells through orifices in the surface piping near the wellhead. Downhole pressure measurements are routine, but are used for injection well testing or under special circumstances in which surface measurements do not provide reliable information about the downhole pressure. A wide variety of pressure sensors are available and suitable for monitoring pressures at the wellhead or in the formation. Continuous data are available and typically transmitted to a central control room. Surface pressure gauges are often connected to shut-off valves that will stop or curtail injection if the pressure exceeds a predetermined safe threshold, or if there is a drop in pressure as a result of a leak. In effect, surface pressures can be used to ensure that downhole pressures do not exceed the threshold of reservoir fracture pressure. A relatively recent innovation, fiber-optic pressure and temperature sensors, is commercially available. Fiber-optic cables are lowered into the wells, connected to sensors, and provide real-time formation pressure and temperature measurements. These new systems are expected to provide more reliable measurements and well control.

The current state of the technology is more than adequate to meet the needs for monitoring injection rates, wellhead, and formation pressures. Combined with temperature measurements, the collected data will provide information on the state of the CO_2 (supercritical, liquid, or gas) and accurate measurement of the amount of CO_2 injected for inventories, reporting, and verification, as well as input to modeling. In the case of the Weyburn project, for example, the gas stream is also analyzed to determine the impurities in the CO_2, thus allowing computation of the volume of CO_2 injected.

5.6.3 Technologies for monitoring subsurface distribution of CO_2

There are a number of techniques that can be used to monitor the distribution and migration of CO_2 in the subsurface. Table 5.4 summarizes these techniques and how they can be applied to CO_2 storage projects. The applicability and sensitivity of these techniques are somewhat site specific.

Detailed descriptions, including limitations and resolution, are provided in Sections 5.6.3.1 and 5.6.3.2.

Table 5.4. Summary of direct and indirect techniques that can be used to monitor CO_2 storage projects. The table includes a list of techniques, the parameters that are measured, and selected examples of how they may be applied to monitor CO_2 storage projects.

5.6.3.1 Direct techniques for monitoring CO_2 migration

Direct techniques for monitoring are limited in availability at present. During CO_2 injection for EOR, the injected CO_2 spreads through the reservoir in a heterogeneous manner, based on permeability variations in the reservoir (Moberg et al., 2003). In the case of CO_2-EOR, once the CO_2 reaches a production well, its produced volume can be readily determined. In the case of Weyburn, the carbon in the injected CO_2 has a different isotopic composition from the carbon in the reservoir (Emberley et al., 2002), so the distribution of the CO_2 can be determined on a gross basis by evaluating the arrival of the introduced CO_2 at different production wells. With multiple injection wells in any producing area, the arrival of CO_2 can only give a general indication of distribution in the reservoir.

A more accurate approach is to use tracers (gases or gas isotopes not present in the reservoir system) injected into specific wells. The timing of the arrival of the tracers at production or monitoring wells will indicate the path the CO_2 is taking through the reservoir. Monitoring wells may also be used to passively record the movement of CO_2 past the well, although it should be noted that the use of such invasive techniques potentially creates new pathways for leakage to the surface. The movement of tracers or isotopically distinct carbon (in the CO_2) to production or monitoring wells provides some indication of the lateral distribution of the CO_2 in a storage reservoir. In thick formations, multiple sampling along vertical monitoring or production wells would provide some indication of the vertical distribution of the CO_2 in the formation. With many wells, and frequently in horizontal wells, the lack of casing (open hole completion) precludes direct measurement of the location of CO_2 influx along the length of the well, although it may be possible to run surveys to identify the location of major influx.

Direct measurement of migration beyond the storage site can be achieved in a number of ways, depending on where the migration takes the CO_2. Comparison between baseline surveys of water quality and/or isotopic composition can be used to identify new CO_2 arrival at a specific location from natural CO_2 pre-existing at that site. Geochemical techniques can also be used to understand more about the CO_2 and its movement through the reservoir (Czernichowski-Lauriol et al., 1996; Gunter et al., 2000; Wilson and Monea, 2005). The chemical changes that occur in the reservoir fluids indicate the increase in acidity and the chemical effects of this change, in particular the bicarbonate ion levels in the fluids. At the surface, direct measurement can be undertaken by sampling for CO_2 or tracers in soil gas and near-surface water-bearing horizons (from existing water wells or new observation wells). Surface CO_2 fluxes may be directly measurable by techniques such as infrared spectroscopy (Shuler and Tang, 2005; Miles et al., 2005; Pickles, 2005).

5.6.3.2 Indirect techniques for monitoring CO_2 migration

Indirect techniques for the measurement of CO_2 distribution in the subsurface include a variety of seismic and nonseismic geophysical and geochemical techniques (Arts and Winthaegen, 2005; Hoversten and Gasperikova, 2005; Benson et al., 2004). Seismic techniques basically measure the velocity and energy absorption of waves, generated artificially or naturally, through rocks. The

transmission is modified by the nature of the rock and its contained fluids. In general, energy waves are generated artificially by explosions or ground vibration. Wave generators and sensors may be on the surface (conventional seismic), or modified with the sensors in wells within the subsurface and the source on the surface (vertical seismic profiling). It is also possible to place both sensors and sources in the subsurface to transmit the wave pulses horizontally through the reservoir (interwell or crosswell tomography). By taking a series of surveys over time, it is possible to trace the distribution of the CO_2 in the reservoir, assuming the free-phase CO_2 volume at the site is sufficiently high to identify from the processed data. A baseline survey with no CO_2 present provides the basis against which comparisons can be made. It would appear that relatively low volumes of free-phase CO_2 (approximately 5% or greater) may be identified by these seismic techniques; at present, attempts are being made to quantify the amount of CO_2 in the pore space of the rocks and the distribution within the reservoir (Hoversten et al., 2003). A number of techniques have been actively tested at Weyburn (Section 5.6.3.3.1), including time-lapse surface 3D seismic (both 3- and 9-component), at one-year intervals (baseline and baseline plus one and two years), vertical seismic profiling, and crosswell (horizontal and vertical) tomography between pairs of wells.

For deep accumulations of CO_2 in the subsurface, where CO_2 density approaches the density of fluids in the storage formation, the sensitivity of surface seismic profiles would suggest that resolution on the order of 2,500 to 10,000 tonnes of free-phase CO_2 can be identified (Myer et al., 2003; Arts et al., 2005; White et al., 2004). At Weyburn, areas with low injection rates (<2% hydrocarbon pore volume) demonstrate little or no visible seismic response. In areas with high injection rates (3-13% hydrocarbon pore volume) significant seismic anomalies are observed. Work at Sleipner shows that the CO_2 plume comprises several distinct layers of CO_2, each up to about 10 m thick. These are mostly beneath the strict limit of seismic resolution, but amplitude studies suggest that layer thicknesses as low as 1 m can be mapped (Arts et al., 2005, Chadwick et al., 2005). Seismic resolution will decrease with depth and certain other rock-related properties, so the above discussion of resolution will not apply uniformly in all storage scenarios. One possible way of increasing the accuracy of surveys over time is to create a permanent array of sensors, or even sensors and energy sources (U.S. Patent 6813566), to eliminate the problems associated with surveying of locations for sensors and energy sources.
For CO_2 that has migrated even shallower in the subsurface, its gas-like properties will vastly increase the detection limit; hence, even smaller threshold levels of resolution are expected. To date, no quantitative studies have been performed to establish precise detection levels. However, the high compressibility of CO_2 gas, combined with its low density, indicate that much lower levels of detection should be possible.

The use of passive seismic (microseismic) techniques also has potential value. Passive seismic monitoring detects microseismic events induced in the reservoir by dynamic responses to the modification of pore pressures or the reactivation or creation of small fractures. These discrete microearthquakes, with magnitudes on the order of -4 to 0 on the Richter scale (Wilson and Monea, 2005), are picked up by static arrays of sensors, often cemented into abandoned wells. These microseismic events are extremely small, but monitoring the microseismic events may allow the tracking of pressure changes and, possibly, the movement of gas in the reservoir or saline formation.

Nonseismic geophysical techniques include the use of electrical and electromagnetic (EM) and self-potential (SP) techniques (Benson et al., 2004; Hoversten and Gasperikova, 2005). In addition, gravity techniques (ground or aerially based) can be used to determine the migration of the CO_2 plume in the subsurface. Finally, tiltmeters or remote methods (geospatial surveys from aircraft or

satellites) for measuring ground distortion may be used in some environments to assess subsurface movement of the plume. Tiltmeters and other techniques are most applicable in areas where natural variations in the surface, such as frost heave or wetting/drying cycles, do not mask the changes that occur from pressure changes. Gravity measurements will respond to changes in the subsurface brought on by density changes caused by the displacement of one fluid by another of different density (CO_2 replacing water, for example). Gravity is used with numerical modeling to infer those changes in density that best fit the observed data. The estimations of Benson et al. (2004) suggest that gravity will not have the same level of resolution as seismic, with minimum levels of CO_2 needed for detection on the order of several hundred thousand tonnes (an order of magnitude greater than seismic). This may be adequate for plume movement, but not for the early definition of possible leaks. A seabed gravity survey was acquired at Sleipner in 2002, and a repeat survey is planned for 2005. Results from these surveys have not yet been published.

Electrical and electromagnetic techniques measure the conducting of the subsurface. Conductivity changes created by a change in the fluid, particularly the displacement of high conductivity saline waters with low-conductive CO_2, can be detected by electrical or EM surveys. In addition to traditional electrical or EM techniques, the SP, the natural electrical potential, of the earth can be measured to determine plume migration. The injection of CO_2 will enhance fluid flow in the rock. This flow can produce an electrical potential that is measured against a reference electrode. This technique is low cost, but is also of low resolution. It can, however, be a useful tool for measuring the plume movement. According to Hoversten and Gasperikova (2005), this technique will require more work to determine its resolution and overall effectiveness.

5.6.3.3 Monitoring Case Study: IEA GHG Weyburn Monitoring and Storage Project

At Weyburn (Box 5.3), a monitoring program was added to a commercial EOR project to develop and evaluate methods for tracking CO_2. Baseline data was collected prior to CO_2 injection (beginning in late 2000). These data included fluid samples (water and oil) and seismic surveys. Two levels of seismic surveys were undertaken, with an extensive 3D, 3-component survey over the original injection area, and a detailed 3D, 9-component survey over a limited portion of the injection area. In addition, vertical seismic profiling and crosswell seismic tomography between two vertical or horizontal wells) was undertaken. Passive seismic (microseismic) monitoring has recently been installed at the site. Other monitoring includes surface gas surveys (Strutt et al., 2003) and potable water monitoring (the Weyburn Field underlies an area with limited surface water availability, so groundwater provides the major potable water supply). Injected volumes (CO_2 and water) were also monitored. Any leaks from surface facilities are carefully monitored. Additionally, several wells were converted to observation wells to allow access to the reservoir. Subsequently, one well was abandoned, but seismic monitors were cemented into place in the well for passive seismic monitoring to be undertaken.

Since injection began, there has been regular collection and analysis of reservoir fluids. This includes chemical and isotopic analyses of reservoir water samples, as well as maintaining an understanding of miscibility relationships between the oil and the injected CO_2. Several seismic surveys have been conducted (one year and two years after injection of CO_2 was initiated) with the processed data clearly showing the movement of CO_2 in the reservoir. Annual surface analysis of soil gas is also continuing (Strutt et al., 2003), as is the analysis of near-surface water. The analyses are being synthesized to gain a comprehensive knowledge of CO_2 migration in the reservoir, understand geochemical interactions with the reservoir rock, and clearly identify the integrity of the reservoir as a container for long-term storage. Additionally, there is a program to evaluate the potential role of existing active and abandoned wells in leakage. This includes an analysis of the

age of the wells, the use of existing information on cement type and bonding effectiveness, and work to better understand the effect of historical and changing fluid chemistry on the cement and steel casing of the well.

The Weyburn summary report (Wilson and Monea, 2005) describes the overall results of the research project, in particular the effectiveness of the seismic monitoring for determining the spread of CO_2 and the geochemical analysis for determining when CO_2 was about to reach the production wells. Geochemical data also help explain the processes under way in the reservoir itself and the time required to establish a new chemical equilibrium. Figure 5.24 illustrates the change in the chemical composition of the formation water, which forms the basis for assessing the extent to which solubility and mineral trapping will contribute to long-term storage security (Perkins et al., 2005). The initial change in $\delta^{13}C_{HCO3}$ is the result of the supercritical CO_2 dissolving into the water. This change is then muted by the short-term dissolution of reservoir carbonate minerals, as indicated by the increase of calcium concentration, shown in Figure 5.24. In particular, the geochemistry confirms the storage of CO_2 in water in the bicarbonate phase and also CO_2 in the oil phase.

Figure 5.24. The produced water chemistry prior to CO_2 injection, and the produced water chemistry after 12 months and 36 months of injection at Weyburn has been contoured based on fluid samples taken at various production wells. The black dots show the location of the sample wells: (a) $\delta 13CHCO_3$ in the produced water, showing the effect of supercritical CO_2 dissolution and mineral reaction; (b) Calcium concentrations in the produced water showing the result of mineral dissolution (after Perkins et al., 2005).

5.6.4 Technologies for monitoring injection well integrity

There are a number of standard technologies for monitoring the integrity of active injection wells. Cement bond logs are used to assess the bond and the continuity of the cement around well casing. Periodic cement bond logs can help detect deterioration in the cemented portion of the well and may also indicate any chemical interaction of the acidized formation fluids with the cement. The initial use of cement bond logs as part of the well-integrity testing can indicate problems with bonding and even the absence of cement.

Prior to converting a well to alternate uses, such as CO_2 injection, the well usually undergoes testing to ensure its integrity under pressure. These tests are relatively straightforward, with the well being sealed top and bottom (or in the zone to be tested), pressured up, and its ability to hold pressure measured. In general, particularly on land, the well will be abandoned if it fails the test, and a new well will be drilled, as opposed to attempting any remediation on the defective well.

Injection takes place through a pipe that is lowered into the well and packed off above the perforations or open-hole portion of the well, to ensure that the injectant reaches the appropriate level. The pressure in the annulus, the space between the casing and the injection pipe, can be monitored to ensure the integrity of the packer, casing, and the injection pipe Changes in pressure or gas composition in the annulus will alert the operator to problems.

As noted above, the injection pressure is carefully monitored to ensure that there are no problems. A rapid increase in pressure could indicate problems with the well, although industry interpretations suggest that it is more likely to be loss of injectivity in the reservoir.

Temperature logs and “noise” logs are also often run on a routine basis to detect well failures in natural gas storage projects. Rapid changes in temperature along the length of the wellbore are

diagnostic of casing leaks. Similarly, "noise" associated with leaks in the injection tubing can be used to locate small leaks (Lippmann and Benson, 2003).

5.6.5 Technologies for monitoring local environmental effects

5.6.5.1 Groundwater

If CO_2 leaks from the deep geological storage formation and migrates upwards into overlying shallow groundwater aquifers, methods are available to detect and assess changes in groundwater quality. Of course, it is preferable to identify leakage shortly after it leaks and long before the CO_2 enters the groundwater aquifer, so that measures can be taken to intervene and prevent further migration (see Section 5.7.6). Seismic monitoring methods, and potentially others (described in Section 5.6.3.2), can be used to identify leaks before the CO_2 reaches the groundwater zone.

Nevertheless, if CO_2 does migrate into a groundwater aquifer, potential impacts can be assessed by collecting groundwater samples and analyzing them for major ions (e.g., Na, K, Ca, Mg, Mn, Cl, Si, HCO_3^- and SO_4^{2-}), pH, alkalinity, stable isotopes (e.g., ^{13}C,^{14}C, ^{18}O, ^{2}H), and gases, including hydrocarbon gases, CO_2 and its associated isotopes (Gunter et al., 1998). Additionally, if shallow groundwater contamination occurs, samples could be analyzed for trace elements such as arsenic and lead, which are mobilized by acidic water (Section 5.5). Methods such as atomic absorbtion and inductively coupled plasma mass spectroscopy (ICPMS) can be used to accurately measure water quality. Less sensitive field tests or other analytical methods are also available (Clesceri et al., 1998). Standard analytical methods are available to monitor all of these parameters, including the possibility of continuous real-time monitoring for some of the geochemical parameters.

Natural tracers (isotopes of C, O, H, and noble gases associated with the injected CO_2) and introduced tracers (noble gases, SF_6, and perfluorocarbons) also may provide insight into the impacts of storage projects on groundwater (Emberley et al., 2002; Nimz and Hudson, 2005). (SF_6 and perfluorocarbons are greenhouse gases with extremely high global warming potentials, and therefore caution is warranted in the use of these gases, should they be released to the atmosphere.) Natural tracers such as C and O isotopes may be able to link changes in groundwater quality directly to the stored CO_2 by "fingerprinting" the CO_2, thus distinguishing storage-induced changes from changes in groundwater quality caused by other factors. Introduced tracers such as perfluorocarbons that can be detected at very low concentrations (1 part per trillion) may also be useful for determining whether CO_2 has leaked and is responsible for changes in groundwater quality. Synthetic tracers could be added periodically to determine movement in the reservoir or leakage paths, while natural tracers are present in the reservoir or introduced gases.

5.6.5.2 Air quality and atmospheric fluxes

Continuous sensors for monitoring CO_2 in air are used in a variety of applications, including HVAC (heating, ventilation, and air conditioning) systems, greenhouses, combustion emissions measurement, and environments in which CO_2 is a significant hazard (such as breweries). Such devices rely on infrared detection principles and are referred to as infrared gas analyzers. These gas analyzers are small and portable and commonly used in occupational settings. Most use nondispersive infrared or Fourier Transform infrared detectors. Both methods use light attenuation by CO_2 at a specific wavelength, usually 4.26 microns. For extra assurance and validation of real-time monitoring data, U.S. regulatory bodies, such as NIOSH, OSHA, and the EPA, use periodic concentration measurement by gas chromatography. Mass spectrometry is the most accurate

method for measuring CO_2 concentration, but it is also the least portable. Electrochemical solid-state CO_2 detectors exist, but they are not cost effective at this time (e.g., Tamura et al., 2001).

Common field applications in environmental science include the measurement of CO_2 concentrations in soil air, flux from soils, and ecosystem-scale carbon dynamics. Diffuse soil flux measurements are made using simple IR analyzers (Oskarsson et al., 1999). The USGS measures CO_2 flux on Mammoth Mountain, in Califonia (Sorey et al., 1996; USGS 2001b). Biogeochemists studying ecosystem-scale carbon cycling use CO_2 detectors on 2-5 m tall towers with wind and temperature data to reconstruct average CO_2 flux over large areas.

Miles et al. (2005) concluded that eddy covariance is promising for the monitoring of CO_2 storage projects, both for hazardous leaks and for leaks that would damage the economic viability of geological storage. For a storage project of 100 Mt, Miles et al. (2005) estimates that for leakage rates of 0.01%/yr, fluxes will range from 1 to 10^4 times the magnitude of typical ecological fluxes (depending on the size of the area over which CO_2 is leaking). Note that a leakage rate of 0.01% per year is equivalent to a fraction retained of 90% over 1,000 years. This should easily be detectable if background ecological fluxes are measured in advance to determine diurnal and annual cycles. However, with the technology currently available to us, quantification of leakage rates for the purposes of tracking returns to the atmosphere is likely to be more of a challenge than identifying leaks in the storage reservoir.

Satellite-based remote sensing of CO_2 releases to the atmosphere may also be possible, but remains challenging because of the long path length through the atmosphere over which CO_2 is measured, and because of the inherent variability of atmospheric CO_2. Infrared detectors measure average CO_2 concentration over a given path length, so a diffuse or low-level leak viewed through the atmosphere by satellite would be undetectable. As an example, even large CO_2 seeps, such as that at Mammoth Mountain, are difficult to identify today (Martini and Silver, 2002; Pickles, 2005). Airplane-based measurement using this same principle may be possible. Carbon dioxide has been measured either directly in the plume by a separate IR detector, or calculated from SO_2 measurements and direct ground sampling of the SO_2/CO_2 ratio for a given volcano or event (Hobbs et al., 1991; USGS, 2001b). Remote-sensing techniques currently under investigation for CO_2 detection are LIDAR (light detection and range-finding), a scanning airborne laser, and DIAL (differential absorption LIDAR), which looks at reflections from multiple lasers at different frequencies (Hobbs et al., 1991, Menzies et al., 2001).

In summary, occupational safety monitoring of CO_2 is well established. On the other hand, while some promising technologies are under development for environmental monitoring and leak detection, measurement and monitoring approaches on the temporal and space scales relevant to geological storage need improvement to be truly effective.

5.6.5.3 Ecosystems

The health of terrestrial and subsurface ecosystems can be determined directly by measuring the productivity and biodiversity of flora and fauna, and in some cases (such as at Mammoth Mountain in California) indirectly by using remote-sensing techniques such as hyperspectral imaging (Martini and Silver, 2002; Pickles, 2005; Onstott, 2005). In many areas with natural CO_2 seeps, even those with very low CO_2 fluxes, seeps are generally quite conspicuous features. They are easily recognized in populated areas, both in agriculture and natural vegetation, by reduced plant growth and the presence of precipitants of minerals leached from rocks by acidic water. Therefore, any conspicuous site could be quickly and easily checked for excess CO_2 concentrations without any

large remote-sensing ecosystem studies or surveys. However, in desert environments where vegetation is sparse, direct observation may not be possible. In addition to direct ecosystem observations, analyses of soil gas composition and soil mineralogy can be used to indicate the presence of CO_2 and its impact on soil properties. Detection of elevated concentrations of CO_2 or evidence of excessive soil weathering would indicate the potential for ecosystem impacts.

For aquatic ecosystems, water quality, and in particular low pH, would provide a diagnostic for potential impacts. Direct measurements of ecosystem productivity and biodiversity can also be obtained using standard techniques developed for lakes and marine ecosystems. See Chapter 6 for additional discussion about the impact of elevated CO_2 concentrations on marine environments.

5.6.6 Monitoring network design

There are currently no standard protocols or established network designs for monitoring leakage of CO_2. Monitoring network design will depend on the objectives and requirements of the monitoring program, which will be determined by regulatory requirements and perceived risks posed by the site (Chalaturnyk and Gunter, 2005). For example, current monitoring for EOR is designed to assess the sweep efficiency of the solvent flood and to deal with health and safety issues. In this regard, the monitoring designed for the Weyburn Project uses seismic surveys to determine the lateral migration of CO_2 over time. This is compared with the simulations undertaken to design the operational practices of the CO_2 flood. For health and safety, the program is designed to test groundwater for contamination and to monitor for gas buildup in working areas of the field to ensure worker safety. The surface procedure also uses pressure monitoring to ensure that the fracture pressure of the formation is not exceeded (Chalaturnyk and Gunter, 2005).

The Weyburn Project is designed to assess the integrity of an oil reservoir for long-term storage of CO_2 (Wilson and Monea, 2005). In this regard, the demonstrated ability of seismic surveys to measure migration of CO_2 within the formation is important, but in the long term it may be more important to detect CO_2 that has leaked out of the storage reservoir. In this case, the monitoring program should be designed to achieve the resolution and sensitivity needed to detect CO_2 that has leaked out of the reservoir and is migrating vertically. The use of geochemical monitoring will determine the rate of dissolution of the CO_2 into fluids and the capacity of the minerals within the reservoir to react with the CO_2 and permanently store it. For identification of potential CO_2 leaks, monitoring includes soil gas and groundwater surveys. The soil gas surveys use a grid pattern superimposed on the field to evaluate any change in gas chemistry. Because grid patterns may miss narrow, linear anomalies, the study also looks at the pattern of linear anomalies on the surface that may reflect deeper fault and fracture systems, which could become natural migration pathways.

Current projects, in particular Sleipner and Weyburn, are testing a variety of techniques to determine those that are most effective and least costly. In western Canada, acid-gas injection wells use pressure monitoring and set maximum wellhead injection pressures to ensure that reservoir fracture pressures are not exceeded. No subsurface monitoring is currently required for these projects. Chalaturnyk and Gunter (2005) suggest that an effectively designed monitoring program should allow decisions to be made in the future, based on ongoing interpretation of the data, which should also provide the information necessary to decrease uncertainties over time, or increase monitoring demand if things develop unexpectedly. The corollary to this is that unexpected changes may result in the requirement of increased monitoring until new uncertainties are resolved.

5.6.7 Long-term stewardship monitoring

The purpose of long-term monitoring is to identify movement of CO_2 that may lead to releases that could impact long-term storage security and safety, as well as trigger the need for remedial action. Long-term monitoring can be accomplished using the same suite of monitoring technologies used during the injection phase. However, at the present time, there are no established protocols for what kind of monitoring will be required, by whom, for how long, and with what purpose. Geological storage of CO_2 may persist over many millions of years. The long duration of storage raises some questions about long-term monitoring - an issue that is also addressed in Section 5.8.

Several studies have attempted to address some of these issues. Keith and Wilson (2002) have proposed that governments assume responsibility for monitoring after the active phase of the storage project is over, as long as all regulatory requirements have been met during operation. This study did not, however, specify long-term requirements for monitoring. Though perhaps somewhat impractical in terms of implementation, White et al. (2003) suggested that monitoring might be required for thousands of years. An alternative point of view is presented by Chow et al. (2003) and Benson et al. (2004), who suggest that once it has been demonstrated that the plume of CO_2 is no longer moving, further monitoring should not be required. The rationale for this point of view is that long-term monitoring provides little value if the plume is no longer migrating or the cessation of migration can be accurately predicted and verified by a combination of modeling and short- to mid-term monitoring.

If and when long-term monitoring is required, cost-effective, easily deployed methods for monitoring will be preferred. Methods that do not require wells that penetrate the plume will be desirable, because they will not increase the risk of leakage up the monitoring well itself. There are technologies available today, such as 3D seismic imaging, which can provide satisfactory images of CO_2 plume location. While seismic surveys are perceived to be costly, a recent study by Benson et al. (2004) suggests that this may be a misconception and indicates that monitoring costs on a discounted basis (10% discount rate) are likely to be no higher than U.S. $0.10 per tonne of CO_2 stored. However, seismic imaging has its limitations, as is evidenced by continued drilling of nonproductive hydrocarbon wells, but confidence in its ability to meet most, but not all, of the needs of monitoring CO_2 storage projects is growing. Less expensive and more passive alternatives that could be deployed remotely, such as satellite-based systems, may be desirable, but are not currently able to track underground migration. However, if CO_2 has seeped to the surface, associated vegetative stress can be detected readily in some ecosystems (Martini and Silver, 2002).

Until long-term monitoring requirements are established (Stenhouse et al., 2005), it is not possible to evaluate which technology or combination of technologies for monitoring will be needed or desired. However, suffice it to say that today's technology could be deployed to continue monitoring the location of the CO_2 plume over very long time periods with sufficient accuracy to assess the risk of the plume intersecting potential pathways, natural or human, out of the storage site into overlying zones. If CO_2 escapes from the primary storage reservoir with no prospect of remedial action to prevent leakage, technologies are available to monitor the consequent environmental impact on groundwater, soils, ecosystems, and the atmosphere.

5.6.8 Verification of CO_2 injection and storage inventory

Verification as a topic is often combined with Monitoring such as in the Storage, Monitoring and Verification (SMV) project of the Carbon Capture Project (CCP) or the Measurement, Monitoring and Verification (MMV) subsection of the DOE-NETL Carbon Sequestration Technology

Roadmap and Program Plan (NETL, 2002). In view of this frequently-used combination of terms, there is some overlap in usage between the terms Verification and Monitoring. For this report, "Verification" is defined as the set of activities used for assessing the amount of CO_2 that is stored underground and for assessing how much, if any, is leaking back into the atmosphere.

No standard protocols have been developed specifically for verification of geological storage. However, experience at the Weyburn and Sleipner projects has demonstrated the utility of various techniques for most if not all aspects of verification (Wilson and Monea, 2005; Sleipner Best Practice Manual, 2004). At the very least, verification will require measurement of the quantity of CO_2 stored. Demonstrating that it remains within the storage site, from both a lateral and vertical migration perspective, is likely to require some combination of models and monitoring. Requirements may be site specific, depending on the regulatory environment, requirements for economic instruments, and the degree of risk of leakage. The oversight for verification may be handled by regulators, either directly or by independent third parties contracted by regulators under national law.

5.7 Risk management, risk assessment, and remediation

What are the risks of storing CO_2 in deep geological formations? Can a geological storage site be operated safely? What are the safety concerns and environmental impact if a storage site leaks? Can a CO_2 storage site be fixed if something does go wrong? These are the questions addressed in this section of the report.

5.7.1 Framework for assessing environmental risks

The environmental impacts arising from geological storage fall into two broad categories: local environmental effects and global effects arising from the release of stored CO_2 to the atmosphere. Global effects may alternatively be viewed as uncertainty in the effectiveness of CO_2 storage. Estimates of the likelihood of release to the atmosphere are discussed below (Section 5.7.3), while discussion on the policy implications of potential release from storage is found elsewhere (Chapters 1, 8, and 9).

Local health, safety, and environmental hazards arise from three distinct causes:

- The direct effects of elevated gas-phase CO_2 concentrations in the shallow subsurface and near-surface environment
- The effects of dissolved CO_2 on groundwater chemistry
- The effects that arise from the displacement of fluids by the injected CO_2

In this section, assessment of possible local and regional environmental hazards is organized by the kind of hazard (e.g., human health and ecosystem hazards are treated separately) and by the underlying physical mechanism (e.g., seismic hazards). For example, the discussion of hazards to groundwater quality includes effects that arise directly from the effect of dissolved CO_2 in groundwater, as well as indirect effects resulting from contamination by displaced brines.

Risks are proportional to the magnitude of the potential hazards and the probability that these hazards will occur. For hazards that arise from locally elevated CO_2 concentrations—in the near-surface atmosphere, soil-gas, or in aqueous solution—the risks depend on the probability of leakage from the deep storage site to the surface. Thus, most of the hazards described in Section 5.7.4 should be weighted by the probability of release described in Section 5.7.3. Regarding those risks associated with routine operation of the facility and well maintenance, such risks are expected to be comparable to CO_2-EOR operations.

There are two important exceptions to the rule that risk is proportional to the probability of release. First, local impacts will be strongly dependent on the spatial and temporal distribution of fluxes and the resulting CO_2 concentrations. Episodic and localized seepage will likely tend to have more significant impacts per unit of CO_2 released than will seepage that is continuous and or spatially dispersed. Global impacts arising from release of CO_2 to the atmosphere depend only on the average quantity released over time scales of decades to centuries. Second, the hazards arising from displacement, such as the risk of induced seismicity, are roughly independent of the probability of release.

Although we have limited experience with injection of CO_2 for the explicit purpose of avoiding atmospheric emissions, a wealth of closely related industrial experience and scientific knowledge exists that can serve as a basis for appropriate risk management. In addition to the discussion in this section, relevant industrial experience has been described in Sections 5.1-5.6.

5.7.2 Processes and pathways for release of CO_2 from geological storage sites

Carbon dioxide that exists as a separate phase (supercritical, liquid, or gas) may escape from formations used for geological storage through the following pathways (Figure 5.25):

1. Through the pore system in low-permeability caprocks such as shales, if the capillary entry pressure at which CO_2 may enter the caprock is exceeded
2. Through openings in the caprock or fractures and faults
3. Through man-made pathways, such as poorly completed and/or abandoned pre-existing wells.

Figure 5.25. Some potential escape routes for CO_2 injected into saline formations.

For onshore storage sites, CO_2 that has leaked may reach the water table and migrate into the overlying vadose zone. This occurrence would likely include CO_2 contact with drinking-water aquifers. Depending on the mineral composition of the rock matrix within the groundwater aquifer or vadose zone, the reaction of CO_2 with the rock matrix could release contaminants. The U.S. Environmental Protection Agency (USEPA) has witnessed problems with projects designed to replenish groundwater with rainfall wherein mineralized (fixed) contaminants were inadvertently mobilized in concentrations so as to cause undesirable contamination.

The vadose zone is only partly saturated with water; the rest of the pore space is filled with soil gas (air). Because it is heavier than air, CO_2 will displace ambient soil gas, leading to concentrations that locally may potentially approach 100% in parts of the vadose zone, even for small leakage fluxes. The dissipating effects of seepage into the surface layer are controlled mostly by pressure-driven flow and diffusion (Oldenburg and Unger, 2003). These occur predominantly in most shallow parts of the vadose zone, leaving the deeper part of the vadose zone potentially subject to accumulation of leaking CO_2. The processes of CO_2 migration in the vadose zone can be modeled, subject to limitations in the characterization of actual complex vadose zone and CO_2 leakage scenarios.

For storage sites that are offshore, CO_2 that has leaked may reach the ocean bottom sediments and then, if lighter than the surrounding water, migrate up through the water column until it reaches the atmosphere. Depending upon the leakage rate, it may either remain as a separate phase or completely dissolve into the water column. When CO_2 dissolves, biological impacts to ocean bottom and marine organisms will be of concern. For those sites where separate-phase CO_2 reaches

the ocean surface, hazards to offshore platform workers may be of concern for very large and sudden release rates.

Once through the vadose zone, escaping CO_2 reaches the surface layer of the atmosphere and the surface environment, where humans and other animals can be exposed to it. Carbon dioxide dispersion and mixing result from surface winds and associated turbulence and eddies. As a result, CO_2 concentrations diminish rapidly with elevation, meaning that ground-dwelling animals are more likely to be affected by exposure than are humans (Oldenburg and Unger, 2004). Calm conditions and local topography capable of containing the dense gas will tend to prevent mixing. But such conditions are the exception, and in general, the surface layer can be counted on to strongly dilute seeping CO_2. Nevertheless, potential concerns related to buildup of CO_2 concentrations on calm days must be carefully considered in any risk assessment of a CO_2 storage site. Additionally, high subsurface CO_2 concentrations may accumulate in basements, subsurface vaults, and other subsurface infrastructures where humans may be exposed to risk.

Carbon dioxide injected into coal seams can only escape if it is in free phase (i.e., not adsorbed onto the coal) via the following pathways (Wo et al., 2005a, b): flow into surrounding strata during injection when high pressures are used to inject CO_2 into low-permeability coal, either where the cleat system reaches the top of the seam or via hydrofractures induced to improve the contact between the cleat system and CBM production wells; through faults or other natural pathways intersecting the coal seam; via poorly abandoned coal or CBM exploration wells; and through man-made pathways such as coal mines or mining-induced subsidence cracks. In general, however, CO_2 retained by sorption onto coal will remain confined to the seam even without caprocks, unless the pressure in the coal seam is reduced (e.g., by mining). Changes in pressure and/or temperature lead to changes in the maximum gas content. If the pressure drops markedly, any excess CO_2 may desorb from the coal and flow freely through cleats.

Injection wells and abandoned wells have been identified as one of the most probable leakage pathways for CO_2 storage projects (Gasda et al., 2004; Benson, 2005). When a well is drilled, a continuous, open conduit is created between the land surface and the deep subsurface. If, at the time of drilling, the operator decides that the target formation does not look sufficiently productive, then the well is abandoned as a "dry hole," in accordance with proper regulatory guidelines. Current guidelines typically require filling sections of the hole with cement (Section 5.4 and Figure 5.19).

Drilling and completion of a well involve not only creation of a hole in the earth, but also the introduction of engineered materials into the subsurface, such as well cements and well casing. The overall effect of well drilling is replacement of small but potentially significant cylindrical volumes of rock, including low-permeability caprock, with man-made materials that have properties different from those of the original materials. A number of possible leakage pathways can occur along abandoned wells, as illustrated in Figure 5.26 (Gasda et al., 2004). These include leakage between the cement and the outside of the casing (Figure 5.26a), between the cement and the inside of the metal casing (Figure 5.26b), within the cement plug itself (Figure 5.26c), through deterioration (corrosion) of the metal casing (Figure 5.26d), deterioration of the cement in the annulus (Figure 5.26e), and leakage in the annular region between the formation and the cement (Figure 5.26f). The potential for long-term degradation of cement and metal casing in the presence of CO_2 is a topic of extensive investigations at this time (e.g., Scherer et al., 2005).

Figure 5.26. Possible leakage pathways in an abandoned well: (a) and (b) between casing and cement wall and plug, respectively; (c) through cement plugs; (d) through casing; (e) through cement wall; and (f) between the cement wall and rock (after Gasda et al., 2004).

Figure 5.27. World oil and gas well distribution and density (courtesy of IHS Energy).

The risk of leakage through abandoned wells is proportional to the number of wells intersected by the CO_2 plume, how deep they are, and the abandonment method used. For mature sedimentary basins, the number of wells in proximity to a possible injection well can be large, on the order of many hundreds. For example, in the Alberta Basin in western Canada, more than 350,000 wells have been drilled. Currently, drilling continues at the rate of approximately 20,000 wells per year. The wells are distributed spatially in clusters, with densities that average around four wells per km^2 (Gasda et al., 2004). Worldwide well densities are provided in Figure 5.27 and illustrate that there are many areas with much lower well density. Nevertheless, the data provided in Figure 5.27 are illustrative of an important point made in Section 5.3—namely that storage security in mature oil and gas provinces may be compromised if a large number of wells penetrate the caprocks. Steps need to be taken to address this potential risk.

5.7.3 Probability of release from geological storage sites

Storage sites will presumably be designed to confine all injected CO_2 for geologic timescales. Nevertheless, experience with engineered systems suggest a small fraction of operational storage sites may release CO_2 to the atmosphere. No existing studies systematically estimate the probability and magnitude of release across a sample of credible geological storage systems. In the absence of such studies, this section synthesizes the lines of evidence that enable rough quantitative estimates of achievable fractions retained in storage. Five kinds of evidence are relevant to assessing storage effectiveness:

1. Data from natural systems, including trapped accumulations of natural gas and CO_2, as well as oil
2. Data from engineered systems, including natural gas storage, gas re-injection for pressure support, CO_2 or miscible hydrocarbon EOR, disposal of acid gases, and disposal of other fluids
3. Fundamental physical, chemical, and mechanical processes regarding the fate and transport of CO_2 in the subsurface
4. Results from numerical models of CO_2 transport
5. Results from current geological storage projects.

Natural systems

Natural systems allow inferences about the quality and quantity of geological formations that could be used to store CO_2. The widespread presence of oil, gas, and CO_2 trapped in formations for many millions of years implies that within sedimentary basins, impermeable formations—caprocks—of sufficient quality to confine CO_2 for geological time periods are present. For example, the ~200 $MtCO_2$ trapped in the Pisgah Anticline, northeast of the Jackson Dome (Mississippi), is thought to have been generated in Late Cretaceous times, more than 65 million years ago (Studlick et al., 1990). Retention times of greater than 10 million years are found in many of the world's petroleum basins (Bradshaw et al., 2005). Therefore evidence from natural systems demonstrates that reservoir seals exist that are able to confine CO_2 for millions of years and longer.

Engineered systems

Evidence from natural gas storage systems enables performance assessments of engineered barriers (wells and associated management and remediation) and of the performance of natural systems that have been altered by pressure cycling (Lippmann and Benson, 2003; Perry, 2005). There are approximately 470 currently operating natural gas storage facilities in the U.S.A. with a total storage capacity exceeding 160 Mt natural gas (Figure 5.12). There have been nine documented

incidents of significant leakage: five were related to wellbore integrity, each of which was resolved by reworking the wells; three arose from leaks in caprocks, two of which were remediated and one of which led to project abandonment. The final incident involved early project abandonment owing to poor site selection (Perry, 2005). There are no estimates of the total volumes of gas lost resulting from leakage across all the projects. In one recent serious example of leakage, involving wellbore failure at a facility in Kansas, the total mass released was about 3,000 tonnes (Lee, 2001), equal to less than 0.002% of the total gas in storage in the U.S.A. and Canada. The capacity-weighted median age of the approximately 470 facilities exceeds 25 years. Given that the Kansas failure was among the worst in the cumulative operating history of gas storage facilities, the average annual release rates, expressed as the fraction of stored gas released per year, are likely below 10^{-5}. While such estimates of the expected (or statistical average) release rates are a useful measure of storage effectiveness, they should not be interpreted as implying that release will be a continuous process.

The performance of natural gas storage systems may be regarded as a lower bound on that of CO_2 storage. One reason for this is that natural gas systems are designed for (and subject to) rapid pressure cycling which increases the probability of caprock leakage. On the other hand, CO_2 will dissolve in pore waters (if present), thereby reducing the risk of leakage. Perhaps the only respect in which gas storage systems present lesser risks is that CH_4 is less corrosive than CO_2 to metallic components, such as well casings. Risks are greater in the case of leakage from natural gas storage sites because of the flammable nature of the gas.

5.7.3.1 Fundamental physical, chemical, and mechanical processes regarding fate and transport of CO_2 in the subsurface

As described in Section 5.2, scientific understanding of CO_2 storage, and in particular performance of storage systems, rest on a large body of knowledge in hydrogeology, petroleum geology, reservoir engineering, and related geosciences. Current evaluation has identified a number of processes that alone or in combination can result in very long-term storage. Specifically, the combination of structural and stratigraphic trapping of separate-phase CO_2 below low-permeability caprocks, residual CO_2 trapping, solubility trapping, and mineral trapping can create secure storage over geological time scales.

5.7.3.2 Numerical simulations of long-term storage performance

Simulations of CO_2 confinement in large-scale storage projects suggest that, neglecting abandoned wells, the movement of CO_2 through the subsurface will be slow. For example, Cawley et al. (2005) studied the effect of uncertainties in parameters, such as the flow velocity in the aquifer and capillary entry pressure into caprock, in their examination of CO_2 storage in the Forties Oilfield in the North Sea. Over the 1,000-year time scale examined in their study, Cawley et al. (2005) found that less than 0.2% of the stored CO_2 enters into the overlying layers, and even in the worse case, the maximum vertical distance moved by any of the CO_2 was less than halfway to the seabed. Similarly, Lindeberg and Bergmo (2003) studied the Sleipner field and found that CO_2 would not begin to migrate into the North Sea for 100,000 years, and that even after a million years, the annual rate of release would be ~10^{-6} of the stored CO_2 per year.

Simulations designed to explore the possible release of stored CO_2 to the biosphere by multiple routes, including abandoned wells and other disturbances, have recently become available as a component of more general risk assessment activities (Section 5.7.5). Two studies of the Weyburn site, for example, assessed the probability of release to the biosphere. Walton et al. (2005) used a fully probabilistic model, with a simplified representation of CO_2 transport, to compute a

probability distribution for the cumulative fraction released to the biosphere. After 5,000 years, Walton et al. found an equal probability that the cumulative amount released would be larger or smaller than 0.1% (the median release fraction) and a 95% probability that less than 1% of the total amount stored would be released. Using a deterministic model of CO_2 transport in the subsurface Zhou et al. (2005) found no release to the biosphere in 5,000 years. While using a probabilistic model of transport through abandoned wells, they found a statistical mean release of 0.001% and a maximum release of 0.14% (expressed as the cumulative fraction of stored CO_2 released over 5,000 years).

In saline formations, or oil and gas reservoirs with significant brine content, much of the CO_2 will eventually dissolve in the brine (Figure 5.7), be trapped as a residual immobile phase (Figure 5.8), or be immobilized by geochemical reactions. The time scale for dissolution is typically short compared to the time for CO_2 to migrate out of the storage formation by other processes (Lindeberg and Bergmo, 2003; Ennis-King and Paterson, 2003; Walton et al., 2005). It is expected that many storage projects could be selected and operated so that a very large fraction of the injected CO_2 will dissolve. Once dissolved, CO_2 can eventually be transported out of the injection site by basin-scale circulation or upward migration, but the time scales (millions of years) of such transport are typically sufficiently long that they can (arguably) be ignored in assessing the risk of leakage.

5.7.3.3 Current CO_2 storage projects

As described in Section 5.1.5, several CO_2 storage projects are now in operation and being carefully monitored. While no leakage of stored CO_2 out of the storage formations has been observed in any of the current projects, time is too short, and overall monitoring too limited, to enable direct empirical conclusions about the long-term performance of geological storage. Rather than providing a direct test of performance, the current projects improve the quality of long-duration performance predictions by testing and sharpening understanding of CO_2 transport and trapping mechanisms.

5.7.3.4 Assessing the ability of operational geological storage projects to retain CO2 for long time periods

Assessment of the fraction retained for geological storage projects is highly site specific, depending on (1) the storage system design, including the geological characteristics of the selected storage site; (2) the injection system and related reservoir engineering; and (3) the methods of abandonment, including the performance of well-sealing technologies. If the above information is available, it is possible to estimate the fraction retained based on the models described in Section 5.4.2 and risk assessment methods described in Section 5.7.5. Therefore, it is also possible, in principle, to estimate the expected performance of an ensemble of storage projects that adhere to design guidelines such as site selection, seal integrity, injection depth, and well closure technologies. Table 5.5 summarizes disparate lines of evidence on the integrity of CO_2 storage systems.

Table 5.5. Summary of evidence forCO_2 retention and release rates.

For large-scale operational CO_2 storage projects, assuming that sites are well selected, designed, operated and appropriately monitored, the balance of available evidence suggests that;

- It is very likely the fraction of stored CO_2 retained is more than 99% over the first 100 years.
- It is likely the fraction of stored CO_2 retained is more than 99% over the first 1000 years.

5.7.4 Possible local and regional environmental hazards

5.7.4.1 Potential hazards to human health and safety

Risks to human health and safety arise (almost) exclusively from elevated CO_2 concentrations in ambient air, either in confined outdoor environments, in caves, or in buildings. Physiological and toxicological responses to elevated CO_2 concentrations are relatively well understood (Appendix AI.4). At concentrations above ~2%, CO_2 has a strong effect on respiratory physiology, and at concentrations above 7-10%, it can cause unconsciousness and death. Exposure studies have not revealed any adverse health effect of chronic exposure to concentrations below 1%.

The principal challenge in estimating the risks posed by CO_2 that might seep from storage sites lies in estimating the spatial and temporal distribution of CO_2 fluxes reaching the shallow subsurface, and in predicting ambient CO_2 concentration resulting from a given CO_2 flux. Concentrations in surface air will be strongly influenced by surface topography and atmospheric conditions. Because CO_2 is 50% denser than air, it tends to migrate downwards, flowing along the ground and collecting in shallow depressions, potentially creating much higher concentrations in confined spaces than in open terrain.

Seepage of CO_2 is not uncommon in regions influenced by volcanism. Naturally occurring releases of CO_2 provide a basis for understanding the transport of CO_2 from the vadose zone to the atmosphere, as well as providing empirical data that link CO_2 fluxes into the shallow subsurface with CO_2 concentrations in the ambient air—and the consequent health and safety risks. Such seeps do not, however, provide a useful basis for estimating the spatial and temporal distribution of CO_2 fluxes leaking from a deep storage site, because (in general) the seeps occur in highly fractured volcanic zones, unlike the interiors of stable sedimentary basins, the likely locations for CO_2 storage (Section 5.3).

Natural seeps are widely distributed in tectonically active regions of the world (Morner and Etiope, 2002). In central Italy, for example, CO_2 is emitted from vents, surface degassing, and diffuse emission from CO_2-rich groundwater. Fluxes from vents range from less than 100 tonnes per day to over 430 tonnes per day, which have shown to be lethal to animal and plants. At Poggio dell'Ulivo, for example, a flux of 200 tonnes per day of CO_2 is emitted from diffuse soil degassing. At least 10 people have died from CO_2 releases in the region of Lazio over the last 20 years.

Natural and engineered analogues show that it is possible, though improbable, that slow releases from CO_2 storage reservoirs will pose a threat to humans. Sudden, catastrophic releases of natural accumulations of CO_2 have occurred, associated with volcanism or subsurface mining activities. Thus, they are of limited relevance to understanding risks arising from CO_2 stored in sedimentary basins. However, mining or drilling in areas with CO_2 storage sites may pose a long-term risk after site abandonment if institutional knowledge and precautions are not in place to avoid accidentally penetrating a storage formation.

5.7.4.2 Hazards to groundwater from CO_2 leakage and brine displacement

Increases in dissolved CO_2 concentration that might occur as CO_2 migrates from a storage reservoir to the surface will alter groundwater chemistry, potentially affecting shallow groundwater used for potable water and industrial and agricultural needs. Dissolved CO_2 forms carbonic acid, altering the pH of the solution and potentially causing indirect effects, including mobilization of (toxic) metals, sulfate, or chloride; and possibly giving the water an odd odor, color, or taste. In the worst case,

contamination might reach dangerous levels, excluding the use of groundwater for drinking or irrigation.

Wang and Jaffé (2004) used a chemical transport model to investigate the effect of releasing CO_2 from a point source at 100 m depth into a shallow water formation that contained a high concentration of mineralized lead (galena). They found that in weakly buffered formations, the escaping CO_2 could mobilize sufficient dissolved lead to pose a health hazard over a radius of a few hundred meters from the CO_2 source. This analysis represents an extreme upper bound to the risk of metal leaching, since few natural formations have mineral composition so susceptible to the effects of CO_2-mediated leaching, and one of the expressed requirements of a storage site is to avoid compromising other potential resources, such as mineral deposits.

The injection of CO_2 or any other fluid deep underground necessarily causes changes in pore-fluid pressures and in the geomechanical stress fields that reach far beyond the volume occupied by the injected fluid. Brines displaced from deep formations by injected CO_2 can potentially migrate or leak through fractures or defective wells to shallow aquifers and contaminate shallower drinking water formations by increasing their salinity. In the worst case, infiltration of saline water into groundwater or into the shallow subsurface could impact wildlife habitat, restrict or eliminate agricultural use of land, and pollute surface waters.

As is the case for induced seismicity, the experience with injection of different fluids provides an empirical basis for assessing the likelihood that groundwater contamination will occur by brine displacement. As discussed in Section 5.5 and shown in Figure 5.23, the current site-specific injection rates of fluids into the deep subsurface are roughly comparable to the rates at which CO_2 would be injected if geological storage were adopted for storage of CO_2 from large scale power plants. Contamination of groundwater by brines displaced from injection wells is rare, and it is therefore expected that contamination arising from large-scale CO_2 storage activities would also be rare. Density differences between CO_2 and other fluids with which we have extensive experience do not compromise this conclusion, because brine displacement is driven primarily by the pressure/hydraulic head differential of the injected CO_2, not by buoyancy forces.

5.7.4.3 Hazards to terrestrial and marine ecosystems

Stored CO_2, and any accompanying substances, may affect the flora and fauna with which it comes into contact. Impacts might be expected on microbes in the deep subsurface, and on plants and animals in shallower soils and at the surface. The remainder of this discussion focuses only on the hazards where exposures to CO_2 do occur. As discussed in Section 5.7.3, the probability of leakage is low. Nevertheless, it is important to understand the hazards should exposures occur.

In the last three decades, microbes dubbed "extremophiles," living in environments where life was previously considered impossible, have been identified in many underground habitats. These microorganisms have limited nutrient supply and exhibit very low metabolic rates (D'Hondt et al., 2002). Recent studies have described populations in deep saline formations (Haveman and Pedersen, 2001), oil and gas reservoirs (Orphan et al., 2000), and sediments up to 850 m below the sea floor (Parkes et al., 2000). The mass of subsurface microbes may well exceed the mass of biota on the earth's surface (Whitman et al., 2001). The working assumption may be that unless there are conditions preventing it, microbes can be found everywhere at the depths being considered for CO_2 storage, and consequently CO_2 storage sites may generally contain microbes that could be affected by injected CO_2.

The effect of CO_2 on subsurface microbial populations is not well studied. A low-pH, high-CO_2 environment may favor some species and harm others. In strongly reducing environments, the injection of CO_2 may stimulate microbial communities that would reduce the CO_2 to CH_4; while in some other reservoirs, CO_2 injection could cause a short-term stimulation of Fe(III)-reducing communities (Onstott, 2005). From an operational perspective, creation of biofilms may reduce the effective permeability of the formation.

Should CO_2 leak from the storage formation and find its way to the surface, it will enter a much more biologically active area. While elevated CO_2 concentrations in ambient air can accelerate plant growth, such fertilization will generally be overwhelmed by the detrimental effects of elevated CO_2 in soils, because CO_2 fluxes large enough to significantly increase concentrations in the free air will typically be associated with much higher CO_2 concentrations in soils. The effects of elevated CO_2 concentrations would be mediated by several factors: the type and density of vegetation; the exposure to other environmental stresses; the prevailing environmental conditions like wind speed and rainfall; the presence of low-lying areas; and the density of nearby animal populations.

The main characteristic of long-term elevated CO_2 zones at the surface is the lack of vegetation. New CO_2 releases into vegetated areas cause noticeable die-off. In those areas where significant impacts to vegetation have occurred, CO_2 makes up about 20-95% of the soil gas, whereas normal soil gas usually contains about 0.2-4% CO_2. Carbon dioxide concentrations above 5% may be dangerous for vegetation, and as concentration approach 20%, CO_2 becomes phytotoxic. Carbon dioxide can cause death of plants through "root anoxia," together with low oxygen concentration (Leone et al., 1977; Flower et al., 1981).

One example of plant die-off occurred at Mammoth Mountain, California, U.S.A., where a resurgence of volcanic activity resulted in high CO_2 fluxes. In 1989, there was a series of small earthquakes near Mammoth Mountain. A year later, 4 ha of pine trees were discovered to be losing their needles, and by 1997, the area of dead and dying trees had expanded to 40 ha (Farrar et al., 1999). Soil CO_2 levels above 10-20% inhibit root development and decrease water and nutrient uptake; soil oil-gas testing at Mammoth Mountain in 1994 discovered soil gas readings of up to 95% CO_2 by volume. Total CO_2 flux in the affected areas averaged about 530 tonnes per day in 1996. Measurements in 2001 showed soil CO_2 levels of 15-90%, with flux rates at the largest affected area (Horseshoe Lake) averaging 90-100 tonnes of CO_2 per day (Rogie et al., 2001; Gerlach et al., 1999). A study of the impact of elevated CO_2 on soils found there was a lower pH and higher moisture content in summer. Wells in the high CO_2 area showed higher levels of silicon, aluminum, magnesium, and iron, consistent with enhanced weathering of the soils. Tree-ring data show that CO_2 releases have occurred prior to 1990 (Cook et al., 2001). Data from airborne remote sensing are now being used to map tree health and measure anomalous CO_2 levels, which may help determine how CO_2 impacts forest ecosystems (Martini and Silver, 2002).

There is no evidence of any terrestrial impact from current CO_2 storage projects. Likewise, there is no evidence from EOR projects that indicate impacts to vegetation such as those described above. However, no systematic studies have occurred to look for terrestrial impacts from current EOR projects.

Natural CO_2 seepage in volcanic regions, therefore, provides examples of possible impacts from leaky CO_2 storage, although (as mentioned in Section 5.5.3.1) seeps in volcanic provinces provide a poor analogue to seepage that would occur from CO_2 storage sites in sedimentary basins. As described above, CO_2 seepage can pose substantial hazards. In the Alban Hills, south of Rome

(Italy), for example, 29 cows and 8 sheep were asphyxiated in several separate incidents between September 1999 and October 2001 (Carapezza et al., 2003). The measured CO_2 flux was ~60 tonnes per day of 98% CO_2 and up to 2% H_2S, creating hazardous levels of each gas in localized areas, particularly in low-wind conditions. The high CO_2 and H_2S fluxes resulted from a combination of magmatic activity and faulting.

Human activities have caused detrimental releases of CO_2 from the deep subsurface. In the late 1990s, vegetation died off above an approximately 3 km deep geothermal field being exploited for a 62 MW power plant, in Dixie Valley, Nevada, U.S.A. (Bergfeld et al., 2001). A maximum flux of 570 g CO_2/m^2 per day was measured, as compared to a background level of 7 g/m^2 per day. By 1999, CO_2 flow in the measured area ceased, and vegetation began to return.

The relevance of these natural analogues to leakage from CO_2 storage varies. For examples presented here, the fluxes, and therefore the risks, are much higher than might be expected from a CO_2 storage facility: the annual flow of CO_2 at the Mammoth Mountain site is roughly equal to a release rate on the order of 0.2% per year from a storage site containing 100 $MtCO_2$. This corresponds to a fraction retained of 13.5% over 1,000 years and, thus, is not representative of a typical storage site.

Seepage from offshore geological storage sites may pose a hazard to benthic environments and organisms as the CO_2 moves from deep geological structures through benthic sediments to the ocean. While leaking CO_2 might be hazardous to the benthic environment, the seabed and overlying seawater can also provide a barrier, reducing the escape of seeping CO_2 to the atmosphere. These hazards are distinctly different from the environmental effects of the dissolved CO_2 on aquatic life in the water column, which are discussed in Chapter 6. No studies specifically address the environmental effects of seepage from subseabed geological storage sites.

5.7.4.4 Induced seismicity

Underground injection of CO_2 or other fluids into porous rock at pressures substantially higher than formation pressures can induce fracturing and movement along faults see Section 5.5. 4 and Healy et al., 1968; Gibbs et al., 1973; Raleigh et al., 1976; Streit et al., 2005; Sminchak et al., 2002; Wo et al., 2005b). Induced fracturing and fault activation may pose two kinds of risks. First, brittle failure and associated microseismicity induced by overpressuring can create or enhance fracture permeability, thus providing pathways for unwanted CO_2 migration (Streit and Hillis, 2003). Second, fault activation can, in principle, induce earthquakes large enough to cause damage (e.g., Healy et al., 1968).

Fluid injection into boreholes can induce microseismic activity, as for example at the Rangely Oil Field in Colorado, U.S.A. (Gibbs et al., 1973; Raleigh et al., 1976), in test sites such as the drillholes of the German continental deep drilling program (Shapiro et al., 1997; Zoback and Harjes, 1997) or the Cold Lake Oil Field, Alberta, Canada (Talebi et al., 1998). Deep-well injection of waste fluids may induce earthquakes with moderate local magnitudes (M_L), as suggested for the 1967 Denver earthquakes (M_L of 5.3) (Healy et al., 1968; Wyss and Molnar, 1972) and the 1986/87 Ohio earthquakes (M_L of 4.9) (Ahmad and Smith, 1988) in the U.S.A. Seismicity induced by fluid injection is usually assumed to result from increased pore-fluid pressure in the hypocentral region of the seismic event (e.g., Healy et al., 1968; Talebi et al., 1998).

Readily applicable methods exist to assess and control induced fracturing or fault activation (see section 5.5.4). Several geomechanical methods have been identified for assessing the stability of

faults and estimating maximum sustainable pore-fluid pressures for CO_2 storage (Streit and Hillis, 2003). Such methods, which require the determination of *in situ* stresses, fault geometries, and relevant rock strengths, are based on brittle failure criteria and have been applied to several study sites for potential CO_2 storage (Rigg et al., 2001; Gibson-Poole et al., 2002).

The monitoring of microseismic events, especially in the vicinity of injection wells, can indicate whether pore fluid pressures have locally exceeded the strength of faults, fractures, or intact rock. Acoustic transducers that record microseismic events in monitoring wells of CO_2 storage sites can be used to provide real-time control to keep injection pressures below the levels that induce seismicity. Together with the modeling techniques mentioned above, monitoring can reduce the chance of damage to top seals and fault seals (at CO_2 storage sites) caused by injection-related pore-pressure increases.

Fault activation is primarily dependent on the extent and magnitude of the pore-fluid-pressure perturbations. It is therefore determined more by the quantity and rate than by the kind of fluid injected. Estimates of the risk of inducing significant earthquakes may therefore be based on the diverse and extensive experience with deep-well injection of various aqueous and gaseous streams for disposal and storage. Perhaps the most pertinent experience is the injection of CO_2 for EOR; about 30 $MtCO_2$/yr is now injected for EOR worldwide, and the cumulative total injected exceeds 0.5 $GtCO_2$, yet there have been no significant seismic effects attributed to CO_2-EOR. In addition to CO_2, other injected fluids include brines associated with oil and gas production (>2 Gt per year); Floridan aquifer wastewater (>0.5 Gt per year); hazardous wastes (>30 Mt per year); and natural gas (>100 Mt per year) (Wilson et al., 2003).

While few of these cases may precisely mirror the conditions under which CO_2 would be injected for storage (the peak pressures in CO_2-EOR may, for example, be lower than would be used in formation storage), these quantities compare to, or exceed, plausible flows of CO_2 into storage. For example, in some cases such as the Rangely Oil Field, U.S.A., current reservoir pressures even exceed the original formation pressure (Raleigh et al., 1976). Thus, they provide a substantial body of empirical data upon which to assess the likelihood of induced seismicity resulting from fluid injection. The fact that only a few individual seismic events associated with deep-well injection have been recorded suggests that the risks are low. Perhaps more importantly, these experiences demonstrate that the regulatory limits imposed on injection pressures are sufficient to avoid significant injection-induced seismicity. Designing CO_2 storage projects to operate within these parameters should be possible. Nevertheless, because formation pressures in CO_2 storage formations may exceed those found in CO_2-EOR projects, more experience with industrial scale CO_2 storage projects will be needed to fully assess risks of microseismicity.

5.7.4.5 Implications of gas impurity

Under some circumstances, H_2S, SO_2, NO_2, and other trace gases may be stored along with CO_2 (Bryant and Lake, 2005; Knauss et al., 2005), and this may affect the level of risk. For example, H_2S is considerably more toxic than CO_2, and well blow-outs containing H_2S may present greater risks than from well blow-outs from storage sites that only contain CO_2. Similarly, dissolution of SO_2 in groundwater creates a far stronger acid than does dissolution of CO_2. Hence, the mobilization of metals in groundwater and soils may be higher, leading to greater risk of exposure to hazardous levels of trace metals. While there has not been a systematic and comprehensive assessment of how these additional constituents would impact the risks associated with CO_2 storage, it is worth noting that at Weyburn, one of the most carefully monitored CO_2 injection projects, and one for which a considerable effort has been devoted to risk assessment, the injected

gas contains approximately 2% H_2S (Wilson and Monea, 2005). To date, most risk assessment studies have assumed that only CO_2 is stored; therefore, insufficient information is available to assess the risks associated with gas impurities at the present time.

5.7.5 Risk assessment methodology

Risk assessment aims to identify and quantify potential risks caused by the subsurface injection of CO_2, where risk denotes a combination (often the product) of the probability of an event happening and the consequences of the event. Risk assessment should be an integral element of risk-management activities, spanning site selection, site characterization, storage system design, monitoring, and, if necessary, remediation.

The operation of a CO_2 storage facility will necessarily involve risks arising from the operation of surface facilities such as pipelines, compressors, and wellheads. The assessment of such risks is routine practice in the oil and gas industry, and available assessment methods like hazard and operability and quantitative risk assessment are directly applicable. Assessment of such risks can be made with considerable confidence, because estimates of failure probabilities and the consequences of failure can be based directly on experience. Techniques used for assessment of operational risks will not, in general, be readily applicable to assessment of risks arising from long-term storage of CO_2 underground. However, they are applicable to the operating phase of a storage project. The remainder of this subsection addresses the long-term risks.

Risk assessment methodologies are diverse; new methodologies arise in response to new classes of problems. Because analysis of the risks posed by geological storage of CO_2 is a new field, no well-established methodology for assessing such risks exists. Methods dealing with the long-term risks posed by the transport of materials through the subsurface have been developed in the area of hazardous and nuclear waste management (Hodgkinson and Sumerling, 1990; North, 1999). These techniques provide a useful basis for assessing the risks of CO_2 storage. Their applicability may be limited, however, because the focus of these techniques has been on assessing the low-volume disposal of hazardous materials, whereas the geological storage of CO_2 is high-volume disposal of a material that involves comparatively mild hazards.

There are several substantial efforts under way to assess the risks posed by particular storage sites (Gale, 2003). These risk assessment activities cover a wide range of reservoirs, use a diversity of methods, and consider a very wide class of risks. The description of a representative selection of these risk assessment efforts is summarized in Table 5.6.

Table 5.6. Representative selection of risk assessment models and efforts.

The development of a comprehensive catalogue of the risks, and of the mechanisms that underlie them, provides a good foundation for systematic risk assessment. Many of the ongoing risk assessment efforts are now cooperating in the identification, classification, and screening of all factors that may influence the safety of storage facilities, using the features, events, and processes (FEP) methodology. In this context, *features* includes a list of parameters, such as storage reservoir permeability, caprock thickness, and number of injection wells. *Events* includes processes such as seismic events, well blow-outs, and penetration of the storage site by new wells. *Processes* refers to the physical and chemical processes, such as multiphase flow, chemical reactions, and geomechanical stress changes that influence storage capacity and security. FEP databases tie information on individual FEP's to relevant literature and allow classification with respect to likelihood, spatial scale, time scale, etc. However, there are alternative approaches.

Most risk assessments involve use of scenarios that describe possible future states of the storage facility and events that result in leakage of CO_2 or other risks. Each scenario may be considered as an assemblage of selected FEPs. Some risk assessments define a reference scenario that represents the most probable evolution of the system. Variant scenarios are then constructed with alternative FEPs. Various methods are employed to structure and rationalize the process of scenario definition in an attempt to reduce the role of subjective judgments in determining the outcomes.

Scenarios are the starting-points for the selection and development of mathematical-physical models (Section 5.4.2). Such performance assessment models may include representations of all relevant components including the stored CO_2, the reservoir, the seal, the overburden, the soil, and the atmosphere. Many of the fluid-transport models employed for risk assessment are derived from (or identical to) well-established models used in the oil and gas or groundwater management industries (Section 5.4.2). The detail or resolution of various components may vary greatly. Some models are designed to allow explicit treatment of uncertainty in input parameters (Wildenborg et al., 2005a; Stenhouse et al., 2005; Saripalli et al., 2003).

Our understanding of abandoned-well behavior over long time scales is at present relatively poor. Several groups are now collecting data on the performance of well construction materials in high-CO_2 environments and building wellbore simulation models that will couple geomechanics, geochemistry, and fluid transport (Scherer et al., 2005; Wilson and Monea, 2005). The combination of better models and new data should enable the integration of physically based predictive models of wellbore performance into larger performance-assessment models, enabling more systematic assessment of leakage from wells.

The parameter values (e.g., permeability of a caprock) and the structure of the performance assessment models (e.g., the processes included or excluded) will both be, in general, uncertain. Risk analysis may or may not treat this uncertainty explicitly. When risks are assessed deterministically, fixed parameter values are chosen to represent the (often unknown) probability distributions. Often the parameter values are selected "conservatively"—that is, they are selected so that risks are overestimated, although in practice such selections are problematic because the relationship between the parameter value and the risk may itself be uncertain.

Wherever possible, it is preferable to treat uncertainty explicitly. In probabilistic risk assessments, explicit probability distributions are used for some (or all) parameters. Methods such as Monte Carlo analysis are then used to produce probability distributions for various risks. The required probability distributions may be derived directly from data or may involve formal quantification of expert judgments (Morgan and Henrion, 1999). In some cases, probabilistic risk assessment may require that the models be simplified because of limitations on available computing resources.

Studies of natural and engineered analogues provide a strong basis for understanding and quantifying the health, safety, and environmental risks that arise from CO_2 that seeps from the shallow subsurface to the atmosphere. Natural analogues are of less utility in assessing the likelihood of various processes that transport CO_2 from the storage reservoir to the near-surface environment. This is because the geological character of such analogues (e.g., CO_2 transport and seepage in highly fractured zones shaped by volcanism) will typically be very different from sites chosen for geological storage. Engineered analogues such as natural gas storage and CO_2-EOR can provide a basis for deriving quantitative probabilistic models of well performance.

Results from actual risk and assessment for CO_2 storage are provided in 5.7.3.

5.7.6 Risk management

Risk management entails the application of a structured process to identify and quantify the risks associated with a given process, to evaluate these, taking into account stakeholder input and context, to modify the process to remove excess risks, and to identify and implement appropriate monitoring and intervention strategies to manage the remaining risks.

For geological storage, effective risk mitigation consists of four interrelated activities:

- Careful site selection, including performance and risk assessment (Section 5.4), and socio-economic and environmental factors
- Monitoring to provide assurance that the storage project is performing as expected and to provide early warning in the event that it begins to leak (Section 5.6)
- Effective regulatory oversight (Section 5.8)
- Implementation of remediation measures to eliminate or limit the causes and impacts of leakage (Section 5.7.7).

Risk management strategies must use the inputs from the risk assessment process, to enable quantitative estimates of the degree of risk mitigation that can be achieved by various measures and to establish an appropriate level of monitoring, with intervention options available if necessary. Experience from natural gas storage projects and disposal of liquid wastes has demonstrated the effectiveness of this approach to risk mitigation (Perry, 2005; Wilson et al., 2003; Apps, 2005).

5.7.7 Remediation of leaking storage projects

Geological storage projects will be selected and operated to avoid leakage. However, in rare cases, leakage may occur and remediation measures will be needed, either to stop the leak or to prevent human or ecosystem impact. Moreover, the availability of remediation options may provide an additional level of assurance to the public that geological storage can be safe and effective. While little effort has focused on remediation options thus far, Benson and Hepple (2005) surveyed the practices used to remediate natural gas storage projects, groundwater, and soil contamination, as well as disposal of liquid waste in deep geological formations. Based on these, remediation options were identified for most of the leakage scenarios that have been identified, namely:

- Leaks within the storage reservoir
- Leakage out of the storage formation up faults and fractures
- Shallow groundwater remediation
- Vadose zone and soil remediation
- Surface fluxes
- CO_2 in indoor air, especially basements
- Surface water.

Identifying options for remediating leakage of CO_2 from active or abandoned wells is particularly important, because they are known vulnerabilities (Gasda et al., 2004; Perry, 2005). Stopping blow-outs or leaks from injection or abandoned wells can be accomplished using standard techniques, such as injecting a heavy mud into the well casing. If the wellhead is not accessible, a nearby well can be drilled to intercept the casing below the ground surface and then pump mud down into the interception well. After control of the well is re-established, the well can be repaired or abandoned. Leaking injection wells can be repaired by replacing the injection tubing and packers. If the annular space behind the casing is leaking, the casing can be perforated to allow injection (squeezing) of cement behind the casing until the leak is stopped. If the well cannot be repaired, it can be abandoned using the procedure outlined in Section 5.5.2.

Table 5.7 provides an overview of the remediation options available for all the leakage scenarios listed above. Some methods are well established, while others are more speculative. Additional detailed studies are needed to further assess the feasibility of applying these to geological storage projects - based on realistic scenarios, simulations, and field studies.

Table 5.7. Compendium of remediation options geological storage projects (after Benson and Hepple, 2005).

5.8 Legal Issues and Public Acceptance

What legal and regulatory issues might be involved in CO_2 storage? How do they differ from one country to the next and from onshore to offshore? What international treaties exist that have bearing on geological storage? How does and how will the public view geological storage? These subjects are addressed in this section, which is primarily concerned with geological storage, both onshore and offshore.

5.8.1 International law

This section considers the legal position of geological CO_2 storage under international law. Primary sources, namely the relevant treaties, provide the basis for any assessment of the legal position. While States, either individually or jointly, apply their own interpretations to treaty provisions, any determination of the "correct" interpretation will fall to the International Court of Justice or an arbitral tribunal in accordance with the dispute settlement mechanism under that treaty.

5.8.1.1 Sources and nature of international obligations

According to general principles of customary international law, States can exercise their sovereignty in their territories and therefore could engage in activities such as the storage of CO_2 (both geological and ocean) in those areas under their jurisdiction. However, if such storage causes transboundary impacts, States have the responsibility to ensure that activities within their jurisdiction or control do not cause damage to the environment of other States or of areas beyond the limits of national jurisdiction.

More specifically, there exist a number of global and regional environmental treaties, notably those on climate change and the law of the sea and marine environment, which, as presently drafted, could be interpreted as relevant to the permissibility of CO_2 storage, particularly offshore geological storage (Table 5.8).

Table 5.8. Main international treaties for consideration in the context of geological carbon dioxide storage (full titles are given in the Glossary).

Before making any assessment of the compatibility of CO_2 storage with the international legal obligations under these treaties, the general nature of such obligations should be recalled—namely that:

a) Obligations under a treaty fall only on the Parties to that treaty.
b) States take such obligations seriously and so will look to the provisions of such treaties before reaching policy decisions.
c) Most environmental treaties contain underlying concepts, such as sustainable development, precautionary approach, or principles, which should be taken into account when applying their provisions.

d) In terms of supremacy of different treaties, later treaties will supersede earlier ones, but this will depend on *lex specialis,* i.e., provisions on a specific subject will supersede general ones (relevant to the relationship between the United Nations Framework Convention on Climate Change (UNFCCC) and its Kyoto Protocol (KP), and the marine treaties).
e) Amendment of treaties, if needed to permit CO_2 storage, requires further negotiations, a minimum level of support for their adoption and subsequent entry into force, and will amend earlier treaties only for those Parties that have ratified the amendments.

5.8.1.2 Key issues in the application of the marine treaties to CO_2 storage

When interpreting the treaties for the purposes of determining the permissibility of CO_2 storage, particularly offshore geological storage, it is important to bear in mind that the treaties were not drafted to facilitate geological storage but to prohibit marine dumping. Issues to bear in mind include:

a) Whether storage constitutes "dumping," i.e., it does not if the placement of the CO_2 is "other than for the purposes of the mere disposal thereof" in accordance with the United Nations Convention on the Law of the Sea (UNCLOS), the London Convention (LC), the London Protocol (LP), and the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR). Alternative scenarios include experiments and storage for the purposes of enhanced oil recovery.
b) Whether CO_2 storage can benefit from treaty exemptions concerning wastes arising from the normal operations of offshore installations (LC/ LP), or as discharges or emissions from them (OSPAR).
c) Is storage in the seabed expressly covered in the treaties or is it limited to the water column (UNCLOS, LC/LP, OSPAR)?
d) Is CO_2 (or the substance captured if containing impurities) an "industrial waste" (LC), "hazardous waste" (Basel Convention), or does the process of its storage constitute "pollution" (UNCLOS), or is it none of these?
e) Does the method of the CO_2 reaching the disposal site involve pipelines, vessels, or offshore structures (LC/LP, OSPAR)?

5.8.1.3 Literature on geological storage under international law

While it is necessary to look at and interpret the treaty provisions themselves to determine the permissibility of CO_2 storage, there are secondary sources that contain States' or authors' individual interpretations of the treaties.

In their analysis, Purdy and Macrory (2004) conclude that since stored CO_2 does not enter the atmosphere, it will not be classed as an "emission" for the purposes of the UNFCCC/KP, but as an "emission reduction." Emission reductions by CO_2 storage are permitted under the UNFCCC/KP, which allows projects that reduce greenhouse gases at the source. However, the authors consider a potential problem in UNFCCC/KP providing for transparent verification of emission reductions, and there could be concerns over permanence, leakage and security.

In terms of marine treaties, and in relation to OSPAR, which applies to the North East Atlantic, a report from the OSPAR "Group of Jurists and Linguists" contains the State Parties' interpretation of OSPAR on the issue of geological (and ocean) offshore storage (OSPAR Commission, 2004). It concludes that, as there is the possibility of pollution or of other adverse environmental effects, the precautionary principle must be applied. More specifically, the report interprets OSPAR as allowing CO_2 placement in the North East Atlantic (including seabed and subsoil) through a *pipeline from land*, provided it does not involve subsequent activities through a vessel or an

offshore installation (e.g., an oil or gas platform). The report states, however, that placement from a vessel is prohibited, unless for the purpose of experimentation (which would then require being carried out in accordance with other relevant provisions of OSPAR). In the case of placement in the OSPAR maritime area from an *offshore installation*, this depends upon whether the CO_2 to be stored results from offshore or land-based activities. In the case of offshore-derived CO_2, experimental placement will again be subject to the Convention's provisions, while placement for EOR, climate change mitigation, or indeed mere disposal will be strictly subject to authorization or regulation. As regards onshore-derived CO_2, only placement for experimental or EOR purposes will be allowed, subject to the same caveats as for offshore-derived CO_2. The report concludes that, since the applicable OSPAR regime is determined by the method and purpose of placement, and not by the effect of placement on the marine environment, the results may well be that placements with different impacts on the environment (for example, placement in the water column and placement in underground strata) may not be distinguished, while different methods of placement having the same impact may be treated differently. A similar analytical exercise concerning the LC/LP has been initiated by Parties to that Convention.

There is uncertainty regarding the extent to which CO_2 storage falls under the jurisdiction of the marine treaties. Some authors argue they will probably not allow such storage, or that the LC (globally) and OSPAR (in the North East Atlantic) could significantly restrict geological offshore storage (Bewers, 2003; Lenstra and van Engelenburg, 2002). Specifically regarding the issues raised above, the following propositions have been suggested:

- The long-term storage of CO_2 amounts to "dumping" under the conventions (Purdy and Macrory, 2004)-if CO_2 were to be injected for an industrial purpose, i.e., EOR, it would not be considered dumping of waste and would be allowed under the LC (Wall et al., 2005).
- CO_2 captured from an oil or natural gas extraction operation and stored offshore in a geological formation would not be considered "dumping" under the LC (Wall et al., 2005).
- There remain some ambiguities in the provisions of some conventions, especially in relation to the option of geological storage under the seabed (Ducroux and Bewers, 2005). UNCLOS provides the international legal basis for a range of future uses for the seafloor that could potentially include geological storage of CO_2 (Cook and Carleton, 2000).
- Under the LC, CO_2 might fall under the "industrial waste" category in the list of wastes prohibited for disposal, while under the LP and OSPAR it would probably not fall under the categories approved for dumping and should therefore be considered as waste and this is prohibited (Purdy and Macrory, 2004).
- If CO_2 is transported *by ship* and then disposed of, either directly from the ship or from an offshore installation, this will be prohibited under the LC/LP (Wall et al., 2005) and OSPAR (Purdy and Macrory, 2004). If CO_2 is transported *by pipeline* to an offshore installation and then disposed of, that would be prohibited under the LC/LP, but not necessarily under OSPAR, where prohibition against dumping only applies to installations carrying out activities concerning hydrocarbons (Purdy and Macrory, 2004). The option of storing CO_2 transported through a pipeline from land appears to remain open under most conventions (Ducroux and Bewers, 2005); the LC/LP apply only to activities using ships or platforms, and contain no further controls governing pipeline discharges from land-based sources. Any such discharges would probably be excluded from control by the LC because it would not involve "disposal at sea" (Wall et al., 2005). Under OSPAR, however, States have general environmental obligations with respect to land-based sources (Purdy and Macrory, 2004) (and discharges from pipelines from land will be regulated, although not prohibited).

5.8.2 National regulations and standards

States can regulate subsurface injection and storage of CO_2 within their jurisdiction in accordance with their national rules and regulations. Such rules and regulations could be provided by the mining laws, resource conservation laws, laws on drinking water, waste disposal, oil and gas production, treatment of high-pressurized gases, and others. An analysis of existing regulations in North America, Europe, Japan, and Australia highlights the lack of regulations that are specifically relevant for CO_2 storage and the lack of clarity relating to post-injection responsibilities (IEA Greenhouse Gas R&D Programme, 2003; IOGCC, 2005).

Presently, CO_2 is injected into the subsurface for EOR and for disposal of acid gas (Section 5.2.5). The majority of these recovery or disposal activities inject relatively small quantities of CO_2 into reasonably well-characterized formations. Generally, the longevity of CO_2 storage underground and the extent of long-term monitoring of the injected fluids are not specified in the regulation of these activities, which are generally regulated under the larger umbrella of upstream oil and gas production and waste disposal regulations that do not specify storage time and need for post-operational monitoring.

In Canada, the practice of deep-well injection of fluids in the subsurface, including disposal of liquid wastes, is legal and regulated. As a result of provincial jurisdiction over energy and mineral resources, there are no generally applicable national laws that specifically regulate deep-well injection of fluids. Onshore CO_2 geological storage would fall under provincial laws and regulations, while offshore storage and in federally administered territories would fall under federal laws and regulations. In the western provinces that are major oil and gas producers, substantive regulations specifically manage the use of injection wells. In Alberta, for example, there are detailed procedural regulations regarding well construction, operation, and abandonment, within which specific standards are delineated for five classes of injection wells (Alberta Energy and Utilities Board, 1994). In Saskatchewan, *The Oil and Gas Conservation Regulations 1985* (with amendments through 2000) prescribe standards for disposal of oil field brine and other wastes. In addition, capture, transportation, and operational injection of fluids, including acid gas and CO_2, are by and large covered under existing regulations, but no regulations are in place for monitoring the fate of the injected fluids in the subsurface and/or for the postabandonment stage of an injection operation.

In the U.S.A., the Safe Drinking Water Act regulates most underground injection activities. The USEPA Underground Injection and Control (UIC) program, created in 1980 to provide minimum standards, helps harmonize regulatory requirements for underground injection activities. The explicit goal of the UIC program is to protect current and potential sources of public drinking water. The Safe Drinking Water Act expressly prohibits underground injection that "endangers" an underground source of drinking water. Endangerment is defined with reference to national primary drinking water regulations and adverse human health effects. For certain types or "classes" of wells, regulations by the USEPA prohibit injection that causes the movement of any contaminant into an underground source of drinking water.

Wells injecting hazardous wastes require the additional development of a no-migration petition to be submitted to the regulators. These petitions place the onus of proof on the project proponent that injected fluid will not migrate from the disposal site for 10,000 years or more. The fluids can exhibit buoyancy effects, as disposed fluids can be less dense than the connate fluids of the receiving formation. Operators are required to use models to demonstrate they can satisfy the "no-migration" requirement over 10,000 years. Wilson et al. (2003) suggests that this process of proving containment could provide a model for long-term storage of CO_2. While detailed

requirements exist for siting, constructing, and monitoring injection well operation, there are no federal requirements for monitoring or verification of the actual movement of fluids within the injection zone, nor are there general requirements for monitoring in overlying zones to detect leakage. However, there are requirements for ambient monitoring in deep hazardous and industrial waste wells, with the degree of rigor varying from state to state.

Vine (2004) provides an extensive overview of environmental regulations that might affect geological CO_2 storage projects in California. Given that a developer may need to acquire up to 15 permits from federal, state, and local authorities, Vine stresses the need for research to quantitatively assess the impacts of regulations on project development.

In Australia, permitting responsibility for onshore oil and gas activities reside with the State Governments, while offshore activities are primarily the responsibility of the Federal Government. A comprehensive assessment of the Australian regulatory regime is under way, but so far only South Australia has adopted legislation regulating the underground injection of gases such as CO_2 for EOR and for storage. Stringent environmental impact assessments are required for all activities that could compromise the quality of surface water or groundwater.

The 25 member states of the European Union (EU) have to ensure that geological storage of CO_2 is in conformity with relevant EU Directives. A number of directives could have an influence on CO_2 geological storage in the EU, notably those on waste (75/442/EEC), landfill (1999/31/EC), water (2000/60/EC), environmental impact assessment (85/337/EEC) and strategic environmental assessment (2001/42/EC). These directives were designed in a situation where CO_2 capture and storage was not taken into account and is not specifically mentioned.

There is one comprehensive Dutch study detailing legal and regulatory aspects of CO_2 underground injection and storage (CRUST Legal Task Force, 2001), including ownership of the stored CO_2, duty of care, liability and claim settlement. It has as its basis the legal situation established by the Dutch Mining Act of 2003 that covers "substances" stored underground and unites previously divided regulation of onshore and offshore activities. Storage is defined as "placing or keeping substances at depth of more than 100 m below the surface of the earth." Legal interpretation indicates that CO_2 intended for storage would have to be treated as waste, because it was collected with the explicit purpose of disposal.

Regulating CO_2 storage presents a variety of challenges: the scale of the activity, the need to monitor and verify containment and any leakage of a buoyant fluid, and the long storage time—all of which require specific regulatory considerations. Additionally, injecting large quantities of CO_2 into saline formations that have not been extensively characterized or may be close to populated areas creates potential risks that will need to be considered. Eventually, linkages between a CO_2 storage program and a larger national and international CO_2 accounting regime will need to be credibly established.

5.8.3 Subsurface property rights

Storage of CO_2 in the subsurface raises several questions: Could rights to pore space be transferred to another party? Who owns CO_2 stored in pore space? How can storage of CO_2 in the pore space be managed so as to assure minimal damage to other property rights (e.g., mineral resources, water rights) sharing the same space? Rights to use subsurface pore space could be granted, separating them from ownership of the surface property. This, for example, appears to apply to most European

countries and Canada, whereas in the U.S.A., while there are currently no specific property-rights issues that could govern CO_2 storage, the rights to the subsurface can be severed from the land.

Scale is also an important issue. Simulations have shown that the areal extent of a plume of CO_2 injected from a 1 GW coal-fired power plant over 30 years into a 100 m thick zone will be approximately 100 km^2 (Rutqvist and Tsang, 2002) and may grow after injection ceases. The approach to dealing with this issue will vary, depending on the legal framework for ownership of subsurface pore space. In Europe, for example, pore space is owned by the State and, therefore, utilization is addressed in the licensing process. In the United States, on the other hand, the determination of subsurface property rights on non-federal lands will vary according to state jurisdiction. In the majority of jurisdictions, the surface owner is entitled to exclusive possession of the space formerly occupied by the subsurface minerals when the minerals are exhausted, i.e., the "pore space." In other jurisdictions, however, no such precedent exists (Wilson, 2004). Some guidance for answering these questions can be found in the property rights arrangements associated with natural gas storage (McKinnon, 1998).

5.8.4 Long-term liability

It is important that liabilities that may apply to a storage project are clear to its proponent, including those liabilities that are applicable after the conclusion of the project. While a White Paper by the European Commission outlines the general approach to environmental liability (COM (2000) 66 final), literature specifically addressing liability regimes for CO_2 storage is sparse. De Figueiredo et al. (2005) propose a framework to examine the implications of different types of liability on the viability of geological CO_2 storage, and stress that the way in which liability is addressed may have a significant impact on costs and on public perception of CO_2 geological storage.

A number of novel issues arise with CO_2 geological storage. In addition to long-term *in situ* risk liability, which may become a public liability after project decommissioning, global risks associated with leakage of CO_2 to the atmosphere may need to be considered. Current injection practices do not require any long-term monitoring or verification regime. The cost of monitoring and verification regimes and risk of leakage will be important in managing liability.

There are also considerations about the longevity of institutions and transferability of institutional knowledge. If long-term liability for CO_2 geological storage is transformed into a public liability, can ongoing monitoring and verification be assured, and who will pay for these actions? How will information on storage locations be tracked and disseminated to other parties interested in using the subsurface? What are the time frames for storage? Is it realistic (or necessary) to put monitoring or information systems in place for hundreds of years?

Any discussion of long-term CO_2 geological storage also involves intergenerational liability, and thus justification of such activities involves an ethical dimension. Some aspects of storage security, such as leakage up abandoned wells, may only be realized over a long time frame, thus posing a risk to future generations. Assumptions on cost, discounting, and the rate of technological progress can all lead to dramatically different interpretations of liability and its importance, and need to be closely examined.

5.8.5 Public perception and acceptance

There is insufficient public knowledge of climate change issues and of the various mitigation options, their potential impact, and their practicality. The study of public perceptions and perceived

acceptability of CO_2 capture and storage is at an early stage with few studies (Curry et al., 2005; Gough et al., 2002; Itaoka et al., 2005; Palmgren et al., 2004; Shackley et al., 2004). Research on perceptions of CO_2 capture and storage is challenging because of (1) the relatively technical and "remote" nature of the issue, with few immediate points of connection in the lay public's frame of reference to many key concepts; and (2) the early stage of the technology, with few examples and experiences in the public domain to draw upon as illustrations.

5.8.5.1 Survey research

Curry et al. (2005) surveyed over 1,200 people representing a general population sample of the U.S.A. They found that less than 4% of the respondents were familiar with the terms *carbon dioxide capture and storage* or *carbon storage*. Moreover, there was no evidence that those who expressed familiarity were any more likely to correctly identify that the problem being addressed was global warming rather than water pollution or toxic waste. The authors also showed that there was a lack of knowledge of other power generation technologies (e.g., nuclear power, renewables) in terms of their environmental impacts and costs. Eurobarometer (2003) made similar findings across the European Union. The preference of the sample for different methods to address global warming (do nothing, expand nuclear power, continue to use fossil fuels with CO_2 capture and storage, expand renewables, etc.) was quite sensitive to information provided on relative costs and environmental characteristics.

Itaoka et al. (2005) conducted a survey of just over 1,000 people in Japan. They found much higher claimed levels of awareness of CO_2 capture and storage (31%) and general support for this mitigation strategy as part of a broader national climate change policy, but generally negative views on specific implementation of CCS. Ocean storage was viewed most negatively, while offshore geological storage was perceived as the least negative. Part of the sample was provided with more information about CO_2 capture and storage, but this did not appear to make a large difference in the response. Factor analysis was conducted and revealed that four factors were important in influencing public opinion—namely, perceptions of the environmental impacts and risks (e.g., leakage), responsibility for reducing CO_2 emissions, the effectiveness of CO_2 capture and storage as a mitigation option, and the extent to which it permits the continued use of fossil fuels.

Shackley et al. (2004) conducted 212 face-to-face interviews at a UK airport regarding offshore geological storage. They found the sample was in general moderately supportive of the concept of CO_2 capture and storage as a contribution to a 60% reduction in CO_2 emissions in the UK by 2050 (the government's policy target). Provision of basic information on the technology increased the support that was given to it, though just under half of the sample were still undecided or expressed negative views. When compared with other mitigation options, support for CO_2 capture and storage increased slightly, though other options (such as renewable energy and energy efficiency) were strongly preferred. On the other hand, CO_2 capture and storage was much preferred to nuclear power or higher energy bills (no information on price or the environmental impact of other options was provided). When asked, unprompted, if they could think of any negative effects of CO_2 capture and storage, half of the respondents' mentioned leakage, while others mentioned associated potential impacts upon ecosystems and human health. Others viewed CO_2 capture and storage negatively on the grounds it was avoiding the real problem, was short-termist, or indicated a reluctance to change.

Huijts (2003) polled 112 individuals living in an area above a gas field in The Netherlands that had experienced two small earthquakes (in 1994 and 2001). She found the sample was mildly positive about CO_2 capture and storage in general terms, but neutral to negative about storage in the

immediate neighborhood. The respondents also thought that the risks and drawbacks were somewhat larger than the benefits to the environment and society. The respondents considered that the personal benefits of CO_2 capture and storage were "small" or "reasonably small." On the basis of her findings, Huijts (2003) observed the storage location could make a large difference to its acceptability; onshore storage below residential areas would probably not be viewed positively, although it has to be borne in mind that the study area had experienced recent earthquakes. Huijts also notes that many respondents (25%) tended to choose a neutral answer to questions about CO_2 capture and storage, suggesting they did not yet have a well-formed opinion.

Palmgren et al. (2004) conducted 18 face-to-face interviews in the Pittsburgh, PA, U.S.A., area, followed by a closed-form survey administered to a sample of 126 individuals. The study found that provision of more information led the survey respondents to adopt a more negative view towards CO_2 capture and storage. The study also found that, when asked in terms of willingness to pay, the respondents were less favorable towards CO_2 capture and storage as a mitigation option than they were to all the other options provided (which were rated, in descending order, as follows: solar, hydro, wind, natural gas, energy efficiency, nuclear, biomass, geological storage, and ocean storage). Ocean storage was viewed more negatively than geological storage, especially after information was provided.

5.8.5.2 Focus-group research

Focus-group research on CO_2 capture and storage was conducted in the UK in 2001 and 2003 (Gough et al., 2002, Shackley et al., 2004). Initial reactions tended to be skeptical; only within the context of the broader discussion of climate change, and the need for large cuts in CO_2 emissions, that opinions become more receptive. Typically, participants in these groups were clear that other approaches such as energy efficiency, demand-reduction measures, and renewable energy should be pursued as a priority, and that CO_2 geological storage should be developed alongside, and not as a straight alternative to, these other options. There was general support for use of CO_2 capture and storage as a "bridging measure" while other zero- or low-carbon energy technologies are developed, or as an emergency stop-gap option if such technologies are not developed in time. There was a moderate level of skepticism among participants towards both government and industry and what may motivate their promotion of CO_2 storage, but there was also some distrust of messages promoted by environmental groups. Levels of trust in key institutions and the role of the media were perceived to have a major influence on how CO_2 capture and storage would be received by the public, a point also made by Huijts (2003).

5.8.5.3 Implications of the research

The existing research described above has applied different methodologies, research designs, and terminology, making direct comparisons impossible. Inconsistencies in results have arisen concerning the effect of providing more detailed information to respondents, and the evaluation of CO_2 capture and storage in general terms and in comparison with other low-carbon mitigation options. Explanations for these differences might include the extent of concern expressed regarding future climate change. Representative samples in the U.S.A. and EU (Curry et al., 2005) and most of the smaller samples (Shackley et al., 2004, Itaoka et al., 2005) find moderate to high levels of concern over climate change, whereas respondents in the Palmgren et al. (2004) study rated climate change as the least of their environmental concerns. A further explanation of the difference in perceptions might be the extent to which perceptions of onshore and offshore geological storage have been distinguished in the research.

From this limited research, it appears that at least three conditions may have to be met before CO_2 capture and storage is considered by the public as a credible technology, alongside other better known options: (1) anthropogenic global climate change has to be regarded as a relatively serious problem; (2) there must be acceptance of the need for large reductions in CO_2 emissions to reduce the threat of global climate change; (3) the public has to accept this technology as a nonharmful and effective option that will contribute to the resolution of (1) and (2). As noted above, many existing surveys have indicated fairly widespread concern over the problem of global climate change and a prevailing feeling that the negative impact outweighs any positive effects (e.g., Kempton et. al., 1995; Poortinga and Pidgeon, 2003). On the other hand, some survey and focus group research suggests widespread acceptance of the above factors amongst the public, in particular the need for large reduction in CO_2 emissions, is sporadic and variable within and between national populations. Lack of knowledge and uncertainty regarding the economic and environmental characteristics of other principal mitigation options have also been identified as an impediment to evaluating the CO_2 capture and storage option (Curry et al., 2005).

Acceptance of the three conditions does not imply support for CO_2 capture and storage. The technology may still be rejected by some as too "end of pipe," treating the symptoms not the cause, delaying the point at which the decision to move away from the use of fossil fuels is taken, diverting attention from the development of renewable energy options, and holding potential long-term risks that are too difficult to assess with certainty. Conversely, there may be little realization of the practical difficulties in meeting existing and future energy needs from renewables. Acceptance of CO_2 capture and storage, where it occurs, is frequently "reluctant" rather than "enthusiastic," and in some cases reflects the perception that CO_2 capture and storage might be required because of failure to reduce CO_2 emissions in other ways. Furthermore, several of the studies above indicate that an "in principle" acceptance of the technology can be very different from acceptance of storage at a specific site.

5.8.5.4 Underground storage of other fluids

Given minimal experience with storage of CO_2, efforts have been made to find analogues that have similar regulatory (and hence public acceptance) characteristics (Reiner and Herzog, 2004). Proposals for underground natural gas storage schemes have generated public opposition in some localities, despite similar facilities operating close by without apparent concern (Gough et al., 2002). Concern regarding the effects of underground natural gas storage upon local property prices and difficult-to-assess risks appear in one case to have been taken up and possibly amplified by the local media. Public opposition to onshore underground storage is likely to be heightened by accidents such as the two deaths from explosions in 2001 in Hutchinson, Kansas (U.S.A.), when compressed natural gas escaped from salt cavern storage facilities (Lee, 2001). However, throughout the world today, there are many hundreds of natural gas storage sites that are evidently acceptable to local communities. There has also been a study of the Underground Injection Control Program in the U.S.A., because of the perceived similarity of the governing regulatory regime (Wilson et al., 2003).

5.9 Costs of geological storage

How much will geological storage cost? What are the major factors driving storage costs? Can costs be offset by enhanced oil and gas production? These questions are covered in this section. It starts with a review of the cost elements and factors that affect storage costs, and then presents estimated costs for different storage options. The system boundary for the storage costs used here is the delivery point between the transportation system and the storage site facilities. It is generally

expected that CO_2 will be delivered as a dense fluid (liquid or supercritical) under pressure at this boundary. The costs of capture, compression, and transport to the site are excluded from the storage costs presented here. The figures presented are levelized costs, which incorporate economic assumptions such as the project lifetime, discount rates, and inflation (see Section 3.7.2.2). They incorporate both capital and operating costs.

5.9.1 Cost elements for geological storage

The major capital costs for CO_2 geological storage are drilling wells, infrastructure, and project management. For some storage sites, there may be in-field pipelines to distribute and deliver CO_2 from centralized facilities to wells within the site. Where required, these are included in storage cost estimates. For EOR, EGR, and ECBM options, additional facilities may be required to handle produced oil and gas. Reuse of infrastructure and wells may reduce costs at some sites. At some sites, there may be additional costs for remediation work for well abandonment that are not included in existing estimates. Operating costs include manpower, maintenance, and fuel. The costs for licensing, geological, geophysical, and engineering feasibility studies required for site selection, reservoir characterization, and evaluation before storage starts are included in the cost estimates. Bock et al. (2003) estimate these as $1.685 million for aquifer and depleted oil and gas field storage case studies in the U.S.A. Characterization costs will vary widely from site to site, depending on the extent of pre-existing data, geological complexity of the storage formations and caprock, and risks of leakage. In addition, to some degree, economics of scale may lower the cost per tonne of larger projects; this possibility has not been considered in these estimates.

Monitoring of storage will add further costs and is usually reported separately from the storage cost estimates in the literature. These costs will be sensitive to the regulatory requirements and duration of monitoring. Over the long term, there may be additional costs for remediation and for liabilities.

The cost of CO_2 geological storage is site specific, which leads to a high degree of variability. Cost depends on the type of storage option (e.g., oil or gas reservoir, saline formation), location, depth and characteristics of the storage reservoir formation, and the benefits and prices of any saleable products. Onshore storage costs depend on the location, terrain, and other geographic factors. The unit costs are usually higher offshore, reflecting the need for platforms or subsea facilities and higher operating costs, as shown in separate studies for Europe (Hendriks et al., 2002) and Australia (Allinson et al., 2003). The equipment and technologies required for storage are already widely used in the energy industries, so that costs can be estimated with confidence.

5.9.2 Cost estimates

There are comprehensive assessments of storage costs for U.S.A., Australia, and Europe (Bock et al., 2003, Allinson et al., 2003, Hendriks et al., 2002). These are based on representative geological characteristics for the regions. In some cases, the original cost estimates include compression and pipeline costs, and corrections have been made to derive storage costs (Table 5.9). These estimates include capital, operating, and site characterization costs, but exclude monitoring costs, remediation, and any additional costs required to address long-term liabilities.

The storage option type, depth, and geological characteristics impact the number, spacing, and cost of wells, as well as the facilities cost. Well and compression costs both increase with depth. Well costs depend on the specific technology, the location, the scale of the operation, and local regulations. The cost of wells is a major component; however, the cost of individual wells ranges from ~$200,000 for some onshore sites (Bock et al. 2003) to $25 million for offshore horizontal wells (Table 5.10; Kaarstad, 2002). Increasing storage costs with depth have been demonstrated

(Hendriks et al., 2002). The geological characteristics of the injection formation are another major cost driver, i.e., the reservoir thickness, permeability, and effective radius that impact the amount and rate of CO_2 injection and therefore the number of wells needed. It is more costly to inject and store other gases (NO_x, SO_x, H_2S) with CO_2 because of their corrosive and hazardous nature, although the capture cost may be reduced (Allinson et al., 2003).

5.9.3 Cost estimates for CO_2 geological storage

This section reviews storage costs for options without benefits from enhanced oil or gas production. It describes the detailed cost estimates for different storage options.

5.9.3.1 Saline formations

Allinson et al. (2003) have made a comprehensive review of storage costs for more than 50 sites around Australia that illustrates the variability that might occur across a range of sites at the national or regional scale. Onshore costs for 20 sites have a median cost of $0.5 per tonne of CO_2 stored, with a range of $0.2-5.1 per tonne of CO_2 stored. The 37 offshore sites have a median value of $3.4 per tonne of CO_2 stored and a range of $0.5-30.2 per tonne of CO_2 stored. This work includes sensitivity studies using Monte Carlo analyses of estimated costs to changes in input parameters. The main determinants of storage costs are reservoir and injection characteristics such as permeability, thickness, and reservoir depth, which impact injection rate and well costs, rather than option type (such as saline formation or depleted field).

Bock et al. (2003) have made detailed cost estimates on a series of cases for storage in onshore saline formations in the U.S.A. Their assumptions on geological characteristics are based on a statistical review of more than 20 different formations. These formations represent wide ranges in depth (700-1,800 m), thickness, permeability, injection rate, and well numbers. The base-case estimate for average characteristics has a storage cost of $0.5 per tonne of CO_2 stored. High and low cost cases representing a range of formations and input parameters are $0.4 and $4.5 per tonne of CO_2 stored. This illustrates the variability resulting from input parameters.

Onshore storage costs for saline formations in Europe at a range of depths from 1,000 to 3,000 m are $1.9-6.2 per tonne of CO_2, with a most likely value of $2.8 per tonne of CO_2 stored (Hendriks et al., 2002). This study also presents estimated costs for offshore storage over the same depth range. These estimates cover reuse of existing oil and gas platforms (Hendriks et al., 2002). The range is $4.7-12.0 per tonne of CO_2 stored, showing that offshore costs are higher than onshore costs.

Table 5.9. Compilation of CO_2 storage cost estimates for different options.

5.9.3.2 Disused oil and gas reservoirs

It has been shown that storage costs in disused oil and gas fields in North America and Europe are comparable to those for saline formations (Bock et al., 2003; Hendriks et al., 2002). Bock et al. (2003) present costs for representative oil and gas reservoirs in the Permian Basin (west Texas, U.S.A.). For disused gas fields, the base-case estimate has a storage cost of $2.4 per tonne of CO_2 stored, with low and high cost cases of $0.5 and 12.2 per tonne of CO_2 stored. For depleted oil fields, the base-case cost estimate is $1.3 per tonne of CO_2 stored, with low and high cost cases of $0.5 and $4.0 per tonne of CO_2 stored. Some reduction in these costs may be possible by reuse of existing wells in these fields, but remediation of abandoned wells would increase the costs if required.

In Europe, storage costs for onshore disused oil and gas fields at depths between 1,000 and 3,000 m are in the range \$1.2-3.8 per tonne of CO_2 stored. The most likely value is \$1.7 per tonne of CO_2 stored. Offshore oil and gas fields at the same depths have storage costs of \$3.8-8.1 per tonne of CO_2 stored (most likely \$6.0 per tonne of CO_2 stored). The costs depend on the depth of the reservoir and reuse of platforms. Disused fields may benefit from reduced exploration and monitoring costs.

5.9.3.3 Representative storage costs

The different studies for saline formations and disused oil and gas fields show a very wide range of costs, \$0.2-30.0 per tonne of CO_2 stored, because of the site-specific nature of the costs. This reflects the wide range of geological parameters that occur in any region or country. In effect, there will be multiple sites in any geographic area with a cost curve, providing increasing storage capacity with increasing cost.

The extensive Australian dataset indicates that storage costs are less than \$5.1 per tonne of CO_2 stored for all the onshore sites and more than half the offshore sites. Studies for the U.S.A and Europe also show that storage costs are generally less than \$8 per tonne of CO_2, except for high-cost cases for offshore sites in Europe and depleted gas fields in the U.S.A. In a recent study, it was suggested that 90% of European storage capacity could be used for costs less that \$2 per tonne of CO_2 (Wildenborg et al., 2005b).

Assessment of these cost estimates indicates that there is significant potential for storage at costs in the range of \$0.5-8 per tonne of CO_2 stored, based on the median, base case, or most likely values presented for the different studies (Table 5.9). These exclude monitoring costs, well remediation, and longer term costs.

5.9.3.4 Investment costs for storage projects

Some information is available on the capital and operating costs of industry capture and storage projects (Table 5.10). At Sleipner, the incremental capital cost for the storage component comprising a horizontal well to inject 1 $MtCO_2$ per year was \$15 million (Torp and Brown, 2005). Note that at Sleipner, CO_2 had to be removed from the natural gas to ready it for sale on the open market. The decision to store the captured CO_2 was at least in part driven by a \$40 per tonne of CO_2 tax on offshore CO_2 emissions. Details of the energy penalty and levelized costs are not available. At the planned Snohvit project, the estimated capital costs for storage are \$48 million for injection of 0.7 million t/year CO_2 (Kaarstad, 2002). This dataset is limited, and there is need for additional data on the actual costs of industry projects.

Table 5.10. Investment costs for industry CO_2 storage projects.

5.9.4 Cost estimates for storage with enhanced oil and gas recovery

The costs of CO_2 geological storage may be offset by additional revenues for production of oil or gas, where CO_2 injection and storage is combined with enhanced oil or gas recovery or ECBM. At present, in commercial EOR and ECBM projects using CO_2 injection, the CO_2 is purchased for the project and is a significant proportion of operating costs. The economic benefits from enhanced production make EOR and ECBM potential early options for CO_2 geological storage.

5.9.4.1 Enhanced oil recovery

The costs of onshore CO_2-flooding EOR projects in North America are well documented (Klins, 1984; Jarrell et al., 2002). Carbon dioxide EOR projects are business ventures to increase oil recovery. Although CO_2 is injected and stored, this is not the primary driver, and EOR projects are not optimized for CO_2 storage.

The commercial basis of conventional CO_2-EOR operations is that the revenues from incremental oil compensate for the additional costs incurred (including purchase of CO_2) and provide a return on the investment. The costs differ from project to project. The capital investment components are compressors, separation equipment and hydrogen sulphide removal, drilling wells, and well conversions and completions. New wells are not required for some projects. Operating costs are the CO_2 purchase price, fuel costs, and field operating costs.

In Texas, the cost of CO_2 purchase ranged from 55 to 75% of the total cost for a number of EOR fields (averaging 68% of total costs) and is a major investment uncertainty for EOR. Tax and fiscal incentives, government regulations, and oil and gas prices are the other main investment uncertainties (e.g., Jarrell et al., 2002).

The CO_2 price is usually indexed to oil prices, with an indicative price of $11.7 per tonne of CO_2 ($0.62/Mscf) at a West Texas Intermediate oil price of $18/barrel , $16.3 per tonne of CO_2 at $25/barrel oil and $32.7 per tonne of CO_2 at $50/barrel oil (Jarrell et al., 2002). The CO_2 purchase price indicates the scale of benefit for EOR to offset CO_2 storage costs.

5.9.4.2 Cost of CO_2 storage with enhanced oil recovery

Recent studies have estimated the cost of CO_2 storage in EOR sites (Bock et al., 2003; Hendriks et al., 2002). Estimates of CO_2 storage costs for onshore EOR options in North America have been made by Bock et al. (2003). These are for a 2 MtCO2 per year storage scenario, based on assumptions and parameters from existing EOR operations and industry cost data. These include estimates of the effectiveness of CO_2 EOR, in terms of CO_2 injected for each additional barrel of oil. The methodology for these estimates of storage costs is to calculate the break-even CO_2 price (0.3t).

Experience from field operations across North America provides information about how much of the injected CO_2 remains in the oil reservoir during EOR. An average of 170 standard m^3 CO_2 of new CO_2 is required for each barrel of enhanced oil production, with a range of 85 (0.15t) to 227 (0.4t) standard m^3 (Bock et al., 2003). Typically, produced CO_2 is separated from the oil and reinjected back underground, which reduces the cost of CO_2 purchases.

The base case for a representative reservoir at 1,219 m, based on average EOR parameters in the U.S.A. with an oil price of $15/barrel, has a net storage cost of $-14.8 per tonne of CO_2 stored. Negative costs indicate the amount of cost reduction that a particular storage option offers to the overall capture and storage system. Low and high cost cases representing a range of CO_2 effectiveness, depth, transport distance and oil price are $-92.0 and $66.7 per tonne of CO_2 stored. The low cost case assumes favorable assumptions for all parameters (effectiveness, reservoir depth, productivity) and a $20/barrel oil price. Higher oil prices, such as the $50 per barrel prices in 2005, will considerably change the economics of CO_2-EOR projects. No published studies are available for these higher oil prices.

Other estimates for onshore EOR storage costs all show potential at negative net costs. These include a range of $-10.5 to 10.5 per tonne of CO_2 stored for European sites (Hendriks et al., 2002).

These studies show that use of CO_2 enhanced oil recovery for CO_2 storage can be a lower cost option than saline formations and disused oil and gas fields.

At present, there are no commercial offshore EOR operations, and limited information is available on CO_2 storage costs for EOR options in offshore settings. Indicative storage cost estimates for offshore EOR are presented by Hendricks et al. (2002). Their range is $-10.5 to +21.0 per tonne of CO_2 stored. For the North Sea Forties Field, it has been shown that CO_2-flooding EOR is technically attractive and could increase oil recovery, although at present it is not economically attractive as a stand-alone EOR project (Espie et al., 2003). Impediments are the large capital requirement required for adaptation of facilities, wells, and flow-lines, as well as tax costs and CO_2 supply. It is noted that the economics will change with additional value for storage of CO_2.

The potential benefit of EOR can be deduced from the CO_2 purchase price and the net storage costs for CO_2-EOR/storage case studies. The indicative value of the potential benefit from enhanced oil production to CO_2 storage is usually in the range of $0-16 per tonne of CO_2. In some cases, there is no benefit from EOR. The maximum estimate of the benefit ranges up to $92 per tonne of CO_2 for a single case study involving favorable parameters. In general, higher benefits will occur at high-oil-price scenarios similar to those that have occurred since 2003 and for highly favorable sites, as shown above. At $50 per barrel of oil, the range may increase up to $30 per tonne of CO_2.

5.9.4.3 Cost of CO_2 storage with enhanced gas recovery

CO_2 enhanced gas recovery is a less mature technology than EOR, and it is not in commercial use. Issues are the cost of CO_2 and infrastructure, concerns about excessive mixing, and the high primary recovery rates of many gas reservoirs. Cost estimates show that CO_2-EGR can provide a benefit of $4 to 16 per tonne of CO_2, depending on the price of gas and the effectiveness of recovery (Oldenburg et al., 2002).

5.9.4.4 Cost of CO_2 storage with enhanced coal bed methane

The injection of CO_2 for ECBM production is an immature technology not yet in commercial use. In CO_2-ECBM, the revenues from the produced gas could offset the investment costs and provide a source of income for investors. Cost data are based on other types of CBM operations that are in use.

There is significant uncertainty in the effectiveness of CO_2 storage in coal beds in conjunction with ECBM, because there is no commercial experience. The suggested metric for CO_2 retention is between 1.5 to 10 standard m^3 of CO_2 per standard m^3 of produced methane. The revenue benefit of the enhanced production will depend on gas prices.

Well costs are a major factor in ECBM because many wells are required. In one recent study for an ECBM project (Schreurs, 2002), the cost per production well was given as approximately $750,000/well, plus $1,500 per meter of in-seam drilling. The cost of each injection well was approximately $430,000.

The IEA (1998) developed a global cost curve for CO_2-ECBM, with storage costs ranging from $-20 to +150 per tonne of CO_2. It concluded that only the most favorable sites, representing less than 10% of global capacity, could have negative costs. Estimates of onshore CO_2-ECBM storage costs in the U.S.A. have been made using the approach described for EOR (Bock et al., 2003). They estimate the effectiveness of ECBM in terms of CO_2 injected for incremental gas produced, ranging from 1.5 to 10 units (base-case value 2) of CO_2 per unit of enhanced methane. Other key inputs are

the gas well production rate, the ratio of producers to injectors, well depth, and the number of wells. The base case, storing 2.1 $MtCO_2$ per year for a representative reservoir at 610 m depth in a newly built facility, requires 270 wells. The assumed gas price is $2.00/MBTU. It has a net storage cost of $-8.1 per tonne of CO_2 stored. Low and high cost cases representing a range of parameters are $-26.4 and $+11.1 per tonne of CO_2 stored. The range of these estimates is comparable to other estimates—for example, those for Canada (Wong et al., 2001) and Europe (Hendriks et al., 2002), $0 to +31.5 per tonne of CO_2. Enhanced CBM has not been considered in detail for offshore situations, and cost estimates are not available.

Only one industrial-scale CO_2-ECBM demonstration project has taken place to date, the Allison project in the U.S.A., and it is no longer injecting CO_2 (Box 5.7). One analysis of the Allison project, which has extremely favorable geological characteristics, suggests the economics of ECBM in the U.S.A. are dubious under current fiscal conditions and gas prices (IEA, 2004). The economic analyses suggest this would be commercial, with high gas prices ~$4/GJ) and a credit of $12-18 per tonne of CO_2. Alternatively, Reeves (2005) used detailed modeling and economic analysis to show a break-even gas price of $2.57/Mbtu, including costs of $5.19 per tonne of CO_2 for CO_2 purchased at the field.

5.9.5 Cost of monitoring

While there has been extensive discussion of possible monitoring strategies in the literature and technologies that may be applicable, there is limited information on monitoring costs. These will depend on the monitoring strategy and technologies used and how these are adapted for the duration of storage projects. Some of the technologies likely to be used are already in widespread use in the oil and gas and CBM industries. The costs of individual technologies in current use are well constrained.

Repeated use of seismic surveys was found to be an effective monitoring technology at Sleipner. Its applicability will vary between options and sites. Seismic survey costs are highly variable, according to the technology used, location and terrain, and complexity. Seismic monitoring costs have been reviewed for an onshore storage project for a 1,000 MW power plant with a 30-year life (Myer et al., 2003). Assuming repeat surveys at 5-year intervals during the injection period, monitoring costs are estimated as $0.03 per tonne of CO_2, suggesting that seismic monitoring may only represent a small fraction of overall storage costs. No discounting was used to develop this estimate.

Benson et al. (2005) have estimated life-cycle monitoring costs for two scenarios: (1) storage in an oil field with EOR and (2) storage in a saline formation. For these scenarios, no explicit leakage was considered. If leakage were to occur, the "enhanced" monitoring program should be sufficient to detect and locate the leakage, and may be sufficient to quantify leakage rates as well. For each scenario, cost estimates were developed for the "basic" and "enhanced" monitoring package. The basic monitoring package included periodic seismic surveys, microseismicity, wellhead pressure, and injection-rate monitoring. The enhanced package included all of the elements of the "basic" package and added periodic well logging, surface CO_2 flux monitoring, and other advanced technologies. For the basic monitoring package, costs for both scenarios are $0.05 per tonne of CO_2, based on a discount rate of 10% ($0.16-$0.19 per tonne of CO_2 undiscounted). The cost for the enhanced monitoring package is $0.069-$0.085 per tonne of CO_2 ($0.27-$0.30 per tonne of CO_2 undiscounted). The assumed duration of monitoring includes the 30-year period of injection, as well as further monitoring after site closure of 20 years for EOR sites and 50 years for saline formations. Increasing the duration of monitoring to 1,000 years increased the discounted cost by

10%. These calculations are made assuming a discount rate of 10% for the first 30 years and a discount rate of 1% thereafter.

5.9.6 Cost of remediation of leaky storage projects

No estimates have been made regarding the costs of remediation for leaking storage projects. Remediation methods listed in Table 5.7 have been used in other applications and, therefore, could be extrapolated to CO_2 storage sites. However, this has not been done yet.

5.9.7 Cost reduction

There is little literature on cost-reduction potential for CO_2 geological storage. Economies of scale are likely to be important (Allinson et al., 2003). It is also anticipated that further cost reduction will be achieved with application of learning from early storage projects, optimization of new projects, and application of advanced technologies—such as horizontal and multilateral wells, which are now widely used in the oil and gas industry.

5.10 Knowledge Gaps

Knowledge regarding CO_2 geological storage is founded on basic knowledge in the earth sciences, on the experience of the oil and gas industry (extending over the last hundred years or more), and on a large number of commercial activities involving the injection and geological storage of CO_2 conducted over the past 10-30 years. Nevertheless, CO_2 storage is a new technology, and many questions remain. Here, we summarize what we know now and what gaps remain.

1. Current storage capacity estimates are imperfect.
   - There is need for more development and agreement on assessment methodologies.
   - There are many gaps in capacity estimates at the global, regional, and local levels.
   - The knowledge base for geological storage is for the most part based on Australian, Japanese, North American, and West European data.
   - There is a need to obtain much more information on storage capacity in other areas, particularly in areas likely to experience the greatest growth in energy use, such as China, Southeast Asia, India, Russia/Former Soviet Union, Eastern Europe, the Middle East, and parts of South America and Southern Africa.
2. Overall, storage science is understood, but there is need for greater knowledge of particular mechanisms, including:
   - The kinetics of geochemical trapping and the long-term impact of CO2 on reservoir fluids and rocks
   - The fundamental processes of CO_2 adsorption and CH_4 desorption on coal during storage operations
3. Available information indicates that geological storage operations can be conducted without presenting any greater risks for health and the local environment than similar operations in the oil and gas industry, when carried out at high-quality and well-characterized sites. However, confidence would be further enhanced by increased knowledge and assessment ability, particularly regarding:
   - Risks of leakage from abandoned wells caused by material and cement degradation
   - The temporal variability and spatial distribution of leaks that might arise from inadequate storage sites
   - Microbial impacts in the deep subsurface
   - Environmental impact of CO_2 on the marine seafloor

- Methods to conduct end-to-end quantitative assessment of risks to human health and the local environment

4. There is strong evidence that storage of CO_2 in geological storage sites will be long term; however, it would be beneficial to have:
   - Quantification of potential leakage rates from a greater number of storage sites
   - Reliable coupled hydrogeological-geochemical-geomechanical simulation models to predict long-term storage performance accurately
   - Reliable probabilistic methods for predicting leakage rates from storage sites
   - Further knowledge of the history of natural accumulations of CO_2
   - Effective and demonstrated protocols for achieving desirable storage duration and local safety
5. Monitoring technology is available for determining the behavior of CO_2 at the surface or in the subsurface; however, there is scope for improvement in the following areas:
   - Quantification and resolution of location and forms of CO2 in the subsurface, using geophysical techniques
   - Detection and monitoring of subaquatic CO_2 seepage
   - Remote-sensing and cost-effective surface methods for temporally variable leak detection and quantification, especially for dispersed leaks
   - Fracture detection and characterization of leakage potential
   - Development of appropriate long-term monitoring approaches and strategies
6. There are mitigation and remediation options and technologies available, but there is no track record of remediation for leaked CO_2. While this could be seen as positive, some stakeholders suggest it might be valuable to have an engineered (and controlled) leakage event that could be used as a learning experience.
7. The potential cost of geological storage is known reasonably well, but:
   - There are only a few experience-based cost data from non-EOR CO_2 storage projects.
   - There is little knowledge of regulatory compliance costs.
   - There is inadequate information on monitoring strategies and requirements, which impact costs.
8. The regulatory and responsibility/liability framework for CO_2 storage is yet to be established or unclear - the following issues need to be considered:
   - The role of pilot and demonstration projects in developing regulations
   - Approaches for verification of CO_2 storage for accounting purposes
   - Approaches to regulatory oversight for selecting, operating, and monitoring CO2 storage sites, both in the short and long term.
   - Clarity on the need for and approaches to long-term stewardship
   - Requirements for decommissioning a storage project

Additional information on all of these topics would improve technologies and decrease uncertainties, but there appear to be no insurmountable technical barriers to an increased uptake of geological storage as a mitigation option.

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Tables

Table 5.1. A selection of current and planned geological storage projects.

Project	Country	Scale of Project	Lead Organizations	Injection Start Date	Approximate average daily injection rate	Total storage t CO_2	Storage typ	Geological storage formation	Age of formation	Lithology	Monitoring
Sleipner	**Norway**	Commercial	Statoil, IEA	1996	3000 t/day	20 Mt planned	Aquifer	Utsira Formation	Tertiary	Sandstone	4D seismic plus gravity
Weyburn	**Canada**	Commercial	EnCana, IEA	May 2000	3-5,000 t/day	20 Mt planned	CO_2-EOR	Midale Formation	Mississippian	Carbonate	Comprehensive
Minami-Nagoaka	**Japan**	Demo	Research Institute of Innovative Technology for the Earth	2002	Max 40 t/day	10000 t planned	Aquifer (Sth. Nagoaka Gas Field)	Haizume Formation	Pleistocene	Sandstone	Crosswell seismic, plus well monitoring
Yubari	**Japan**	Demo	Japanese Ministry of Economy, Trade and Industry	2004	10t/day	200 t Planned	CO_2-ECBM	Yubari Formation (Ishikari Coal Basin)	Tertiary	Coal	Comprehensive
In Salah	**Algeria**	Commercial	Sonatrach, BP, Statoil	2004	3-4000 t/day	17 Mt planned	Depleted hydrocarbon reservoirs	Krechba Formation	Carboniferous	Sandstone	Planned comprehensive
Frio	**U.S.A**	Pilot	Bureau of Economic Geology of the University of Texas	4 - 13 Oct 2004	Approx. 177 t/day for 9 days	1600t	Saline formation	Frio Formation	Tertiary	Brine-bearing sandstone-shale	Comprehensive
K12B	**Netherlands**	Demo	Gaz de France	2004	100 t/day to1000 t/day (2006+)	Approx 8 Mt	Enhanced Gas Recovery	Rotleigendes	Permian	Sandstone	Comprehensive
Fenn Big Valley	**Canada**	Pilot	Alberta Research Council	1998	50 t/day	200 t	CO_2-ECBM	Mannville Group	Cretaceous	Coal	P, T, flow
Recopol	**Poland**	Pilot	TNO-NITG (Netherlands)	2003	1 t/day	10 t	CO_2-ECBM	Silesian Basin	Carboniferous	Coal	
Qinshui Basin	**China**	Pilot	Alberta Research Council	2003	30 t/day	150 t	CO_2-ECBM	Shanxi Formation	Carboniferous-Permian	Coal	P, T, flow
Salt Creek	**U.S.A.**	Commercial	Anadarko	2004	5-6000 t/day	27 Mt	CO_2-EOR	Frontier	Cretaceous	Sandstone	Under development
Planned Projects (2005 onwards)											
Snohvit	**Norway**	Decided Commercial	Statoil	2006	2000 t/day		Saline formation	Tubaen Formation	Lower Jurassic	Sandstone	Under development
Gorgon	**Australia**	Planned Commercial	Chevron	Planned 2009	Approx. 10,000 t/day		Saline formation	Dupuy Formation	Late Jurassic	Massive sandstone with shale seal	Under development
Ketzin	**Germany**	Demo	GFZ Potsdam	2006	100 t/day	60 kt	Saline formation	Stuttgart Formation	Triassic	Sandstone	Comprehensive
Otway	**Australia**	Pilot	CO2CRC	Planned late 2005	160 t/day for 2 years	0.1 Mt	Saline fm and depleted gas field	Waarre Formation	Cretaceous	Sandstone	Comprehensive
Teapot Dome	**U.S.A.**	Proposed Demo	RMOTC	Proposed 2006	170 t/day for 3 onths	10 kt	Saline fm and CO_2-EOR	Tensleep and Red Peak Fm	Permian	Sandstone	Comprehensive
CSEMP	**Canada**	Pilot	Suncor Energy	2005	50 t/day	10 kt	CO_2-ECBM	Ardley Fm	Tertiary	Coal	Comprehensive
Pembina	**Canada**	Pilot	Penn West	2005	50 t/day	50 kt	CO_2-EOR	Cardium Fm	Cretaceous	Sandstone	Comprehensive

Table 5.2. Storage capacity for several geological storage options. The storage capacity includes storage options that are not economical.

Reservoir type	Lower estimate of storage capacity ($GtCO_2$)	Upper estimate of storage capacity ($GtCO_2$)
Oil and gas fields	675[a]	900[a]
Unminable coal seams (ECBM)	3 - 15	200
Deep saline formations	1,000	Uncertain, but possibly 10^4

[a] These numbers would increase by 25% if "undiscovered" oil and gas fields were included in this assessment.

Table 5.3. Types of data that are used to characterize and select geological storage sites.

- Seismic profiles across the area of interest, preferably three-dimensional or closely spaced two-dimensional surveys
- Structure contour maps of reservoirs, seals and aquifers
- Detailed maps of the structural boundaries of the trap where the CO_2 will accumulate, especially highlighting potential spill points
- Maps of the predicted pathway along which the CO_2 will migrate from the point of injection
- Documentation and maps of faults and fault
- Facies maps showing any lateral facies changes in the reservoirs or seals
- Core and drill cuttings samples from the reservoir and seal intervals
- Well logs, preferably a consistent suite, including geological, geophysical, and engineering logs
- Fluid analyses and tests from downhole sampling and production testing
- Oil and gas production data (if a hydrocarbon field)
- Pressure transient tests for measuring reservoir and seal permeability
- Petrophysical measurements, including porosity, permeability, mineralogy (petrography), seal capacity, pressure, temperature, salinity, and laboratory rock strength testing
- Pressure, temperature, water salinity
- *In situ* stress analysis to determine potential for fault reactivation and fault slip tendency, and thus identify the maximum sustainable pore fluid pressure during injection in regard to the reservoir, seal, and faults
- Hydrodynamic analysis to identify the magnitude and direction of water flow, hydraulic interconnectivity of formations, and pressure decrease associated with hydrocarbon production
- Seismological data, geomorphological data and tectonic investigations to indicate neotectonic activity

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Table 5.4. Summary of direct and indirect techniques that can be used to monitor CO_2 storage projects. The table includes a list of techniques, the parameters that are measured, and selected examples of how they may be applied to monitor CO_2 storage projects.

Measurement Technique	Measurement Parameters	Example Applications
Introduced and natural tracers	• Travel time • Partitioning of CO_2 into brine or oil • Identification sources of CO_2	• Tracing movement of CO_2 in the storage formation • Quantifying solubility trapping • Tracing leakage
Water composition	• CO_2, HCO_3^-, CO_3^{2-} • Major ions • Trace elements • Salinity	• Quantifying solubility and mineral trapping • Quantifying CO_2-water-rock interactions • Detecting leakage into shallow groundwater aquifers
Subsurface pressure	• Formation pressure • Annulus pressure • Groundwater aquifer pressure	• Control of formation pressure below fracture gradient • Wellbore and injection tubing condition • Leakage out of the storage formation
Well logs	• Brine salinity • Sonic velocity • CO_2 saturation	• Tracking CO_2 movement in and above storage formation • Tracking migration of brine into shallow aquifers • Calibrating seismic velocities for 3D seismic surveys
Time-lapse 3D seismic imaging	• P and S wave velocity • Reflection horizons • Seismic amplitude attenuation	• Tracking CO_2 movement in and above storage formation
Vertical seismic profiling and crosswell seismic imaging	• P and S wave velocity • Reflection horizons • Seismic amplitude attenuation	• Detecting detailed distribution of CO_2 in the storage formation • Detecting leakage through faults and fractures
Passive seismic monitoring	• Location, magnitude and source characteristics of seismic events	• Development of microfractures in formation or caprock • CO_2 migration pathways
Electrical and electromagnetic techniques	• Formation conductivity • Electromagnetic induction	• Tracking movement of CO_2 in and above the storage formation • Detecting migration of brine into shallow aquifers
Time-lapse gravity measurements	• Density changes caused by fluid displacement	• Detect CO_2 movement in or above storage formation • CO_2 mass balance in the subsurface

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Table 5.4. *Continued.*

Measurement Technique	Measurement Parameters	Example Applications
Land surface deformation	• Tilt • Vertical and horizontal displacement using interferometry and GPS	• Detect geomechanical effects on storage formation and caprock • Locate CO_2 migration pathways
Visible and infrared imaging from satellite or planes	• Hyperspectral imaging of land surface	• Detect vegetative stress
CO_2 land surface flux monitoring using flux chambers or eddy-covariance	• CO_2 fluxes between the land surface and atmosphere	• Detect, locate and quantify CO_2 releases
Soil gas sampling	• Soil gas composition • Isotopic analysis of CO_2	• Detect elevated levels of CO_2 • Identify source of elevated soil gas CO_2 • Evaluate ecosystem impacts

Table 5.5. Summary of evidence for CO_2 retention and release rates.

Kind of evidence	Average annual fraction released[(1)]	Representative references
CO_2 in natural formations	The lifetime of CO_2 in natural formations (exceeding 10 million years in some cases) suggests that the average release fraction less than 10^{-7} per year for CO_2 trapped in sedimentary basins. In highly fractured volcanic systems rate of release can be many orders of magnitude faster.	Stevens et al., 2001a. Baines, SJ., and R.H. Worden, 2001.
Oil and Gas	The presence buoyant fluids that have been trapped for geologic timescales demonstrates the widespread presence of geologic systems (seals and caprock) that are capable of confining gasses with release rates of less than 10^{-7} per year.	Bradshaw et al., 2005.
Natural gas storage	The cumulative experience of natural gas storage systems exceeds 10,000 facility-years and demonstrates that operational engineered storage systems can contain methane with release rates of order 10^{-4} to 10^{-6} per year.	Lippmann and Benson, 2003; Perry, 2005.
Enhanced Oil Recovery	More than 100 $MtCO_2$ has been injected for enhanced oil recovery. Data from the limited number of sites where surface fluxes have been measured suggests that fractional release rates are near zero.	Moritis, G., 2002. Klusmanm, R.W., 2003.
Models of flow through the undisturbed subsurface	Numerical models show that release of CO_2 by subsurface flow though undisturbed geologic media (excluding wells) may be near zero at appropriately selected storage sites and is very likely less than 10^{-6} in the small number of studies that attempted probabilistic estimates.	Walton et al., 2005; Zhou et al 2005; Lindeberg and Bergmo, 2003; Cawley et al, 2005.
Models of flow through wells	Evidence from a small number of risk assessment studies suggests that average release of CO_2 can be on the order 10^{-5} to 10^{-7} per year even in existing oil fields with large numbers of abandoned wells such as Weyburn. Simulations with idealized systems with 'open' wells show that release rates can exceed 10^{-2}, though in practice such wells would presumably be closed as soon as CO_2 was detected.	Walton et al 2005; Zhou et al 2005; Nordbotten et al., 2005b.
Current CO_2 storage projects	Data from current CO_2 storage projects demonstrates that monitoring techniques are able to detect movement of CO_2 in the storage reservoirs. Although no release to the surface has been detected, little can be concluded given the short history and limited number of sites.	Wilson, M.and M. Monea., 2005. Arts et al., 2005. Chadwick, et al., 2005.

Table 5.6. Representative selection of risk assessment models and efforts.

Project title	Description and status
Weyburn/ECOMatters	New model, CQUESTRA, developed to enable probabilistic risk assessment. A simple box model is used with explicit representation of transports between boxes due to failure of wells.
Weyburn/Monitor Scientific	Scenario-based modeling using an industry standard reservoir simulation tool (Eclipse3000) based on a realistic model of known reservoir conditions. Initial treatment of wells involves assigning a uniform permeability.
NGCAS/ECL technology	Probabilistic risk assessment using fault tree and FEP database. Initial study focused on the Forties oil and gas field located offshore in the North Sea. Concluded that flow through caprock transport by advection in formation waters not important, work on assessing leakage due to well failures ongoing.
SAMARCADS (safety aspects of CO_2 storage)	Methods and tools for HSE risk assessment applied to two storage systems, and onshore gas storage facility and an offshore formation.
RITE	Scenario-based analysis of leakage risks in a large offshore formation. Will assess scenarios involving rapid release through faults activated by seismic events.
Battelle	Probabilistic risk assessment of an on-shore formation storage site that is intended to represent the Mountaineer site.
GEODISC	Completed a quantitative risk assessment for four sites in Australia: the Petrel Sub-basin; the Dongra depleted oil and gas field; the offshore Gippsland Basin; and, offshore Barrow Island. Also, produced a risk assessment report that addressed the sociopolitical needs of stakeholders.
UK-DTI	Probabilistic risk assessment of failures in surface facilities using models and operational data. Assessment of risk of release from geological storage using an expert based Delphi process.

Table 5.7. Compendium of remediation options for geological storage projects (after Benson and Hepple, 2005).

Scenario	Remediation Options
Leakage up faults, fractures and spill points	• Lower injection pressure by injecting at a lower rate or through more wells (Buschbach and Bond, 1974). • Lower reservoir pressure by removing water or other fluids from the storage structure • Intersect the leakage with extraction wells in the vicinity of the leak • Create a hydraulic barrier by increasing the reservoir pressure upstream of the leak • Lower the reservoir pressure by creating a pathway to access new compartments in the storage reservoir • Stop injection to stabilize the project • Stop injection, produce the CO_2 from the storage reservoir and reinject it back into a more suitable storage structure
Leakage through active or abandoned wells	• Repair leaking injection wells with standard well recompletion techniques such as replacing the injection tubing and packers • Repair leaking injection wells by squeezing cement behind the well casing to plug leaks behind the casing • Plug and abandon injection wells that can not be repaired by the methods listed above. • Stop blow-outs from injection or abandoned wells using standard techniques to "kill" a well such as injecting a heavy mu into the well casing. After control of the well is reestablished, the recompletion or abandonment practices described abov can be used. If the wellhead is not accessible, a nearby well can be drilled to intercept the casing below the ground surfac and "kill" the well by pumping mud down the interception well (DOGGR, 1974).
Accumulation of CO_2 in the vadose zone and soil gas	• Accumulations of gaseous CO_2 in groundwater can be removed, or at least made immobile, by drilling wells that intersect the accumulations and extract the CO_2. The extracted CO_2 could be vented to the atmosphere or reinjected back into a suitable storage site. • Residual CO_2 that is trapped as an immobile gas phase can be removed by dissolving it in water and extracting it as a dissolved phase through groundwater extraction wells. • CO_2 that has dissolved in the shallow groundwater could be removed, if needed, by pumping to the surface and aerating it to remove the CO_2. The groundwater could then either be used directly, or reinjected back into the groundwater. • If metals or other trace contaminants have been mobilized by acidification of the groundwater, "pump-and-treat" methods can be used to remove them. Alternatively, hydraulic barriers created to immobilize and contain the contaminants by appropriately placed injection and extraction wells. In addition to these active methods of remediation, passive methods that rely on natural biogeochemical processes may also be used.

Table 5.7. *Continued*

Scenario	Remediation Options
Leakage into the vadose zone and accumulation in soil gas (Looney and Falta, 2000)	◦ CO_2 can be extracted from the vadose zone and soil gas using standard vapor extraction techniques from horizontal or vertical wells. ◦ Fluxes from the vadose zone to the ground surface could be decreased or stopped using caps or gas vapor barriers. Pumping below the cap or vapor barrier could be used to deplete the accumulation of CO_2 in the vadose zone. ◦ Since CO_2 is a dense gas it could be collected in subsurface trenches. Accumulated gas could be pumped from the trenche and released to the atmosphere or reinjected back underground. ◦ Passive remediation techniques that rely only on diffusion and "barometric pumping" could be used to slowly deplete one time releases of CO_2 into the vadose zone. This method will not be effective for managing ongoing releases because it is relatively slow. ◦ Acidification of the soils from contact with CO_2 could be remediated by irrigation and drainage. Alternatively, agricultura supplements such as lime could also be used to neutralize the soil.
Large releases of CO_2 to the atmosphere	• For releases inside a building or confined space, large fans could be used to rapidly dilute CO_2 to safe levels. • For large releases spread out over a large area, dilution from natural atmospheric mixing (wind) will be the only practical method for diluting the CO_2. • For ongoing leakage in established areas, risks of exposure to high concentrations of CO_2 in confined spaces (e.g. cellar around a wellhead) or during periods of very low wind, fans could be used to keep the rate of air circulation high enough to ensure adequate dilution.
Accumulation of CO_2 indoor environments with chronic low level leakage	• Slow releases into structures can be eliminated using techniques that have been developed for controlling release of rador and volatile organic compounds into buildings. The two primary methods for managing indoor releases are basement/substructure venting or pressurization. Both would have the effect of diluting the CO_2 before it enters the indoo environment (Gadgil et al., 1994; Fischer et al., 1996).
Accumulation in surface water	• Shallow surface water bodies that have significant turnover (shallow lakes) or turbulence (streams) will quickly release dissolved CO_2 back into the atmosphere. • For deep, stably stratified lakes, active systems for venting gas accumulations have been developed and applied at Lake Nyos and Monoun in Cameroon (http://perso.wanadoo.fr/mhalb/nyos/).

Table 5.8. Main international treaties for consideration in the context of geological carbon dioxide storage (full titles are given in the Glossary).

Treaty	Adoption (Signature)	Entry into Force	Number of Parties/Ratifications
UNFCCC	1992	1994	189
Kyoto Protocol	1997	2005	132[a)]
UNCLOS	1982	1994	145
London Convention	1972	1975	80
London Protocol	1996	No	20[a)] (26)
OSPAR	1992	1998	15
Basel Convention	1989	1992	162

[a)] Several other countries have also announced that their ratification is under way.

Table 5.9. Compilation of CO_2 storage cost estimates for different options.

Storage Options (without Enhanced Oil or Gas Production)							
			$/t CO_2 stored				
Option Type	**On/ Offshore**	**Location**	**Low**	**Mid**	**High**	**Comments**	**Nature of Mid point value**
Saline Formation	Onshore	Australia	0.2	**0.5**	5.1	Statistics for 20 sites[1]	Median
Saline Formation	Onshore	Europe	1.9	**2.8**	6.2	Representative range[2]	Most likely value
Saline Formation	Onshore	USA	0.4	**0.5**	4.5	Low/Base/High cases for USA[3]	Base case for average parameters
Saline Formation	Offshore	Australia	0.5	**3.4**	30.2	Statistics for 34 sites[1].	Median
Saline Formation	Offshore	N. Sea	4.7	**7.7**	12.0	Representative range[2]	Most likely value
Depleted Oil Field	Onshore	USA	0.5	**1.3**	4.0	Low/Base/High cases for USA[3]	Base case for average parameters
Depleted Gas Field	Onshore	USA	0.5	**2.4**	12.2	Low/Base/High cases for USA[3]	Base case for average parameters
Disused Oil or Gas Field	Onshore	Europe	1.2	**1.7**	3.8	Representative range[2]	Most likely value
Disused Oil or Gas Field	Offshore	N. Sea	3.8	**6.0**	8.1	Low/Base/High cases for USA[3]	Most likely value

Notes:

The ranges and Low/Most Likely/High values reported in different studies are all on a different basis. The estimates exclude monitoring costs.

1. Figures from Allinson *et al* (2003) are statistics for multiple cases from different sites in Australia. Low is the minimum value, most likely is median, high is maximum value of all the cases. The main determinants of storage costs are rate of injection and reservoir characteristics such as permeability, thickness, reservoir depth rather than reservoir type (such as saline aquifer, depleted field, and so on). The reservoir type could be high or low cost depending on these characteristics. The figures are adjusted to exclude compression and transport costs.
2. Figures from Hendriks *et al* (2002) are described as a representative range of values for storage options between 1000 and 3000m depth. The full range of costs is acknowledged to be larger than shown. The figures are converted from Euros to US $.
3. Bock *et al* (2003) define a base case, low and high cost cases from analysis of typical reservoirs for US sites. Each case has different depth, reservoir, cost and oil/gas price parameters. The figures are adjusted to exclude compression and transport costs.

Table 5.10. Investment costs for industry CO_2 storage projects.

Project		**Sleipner**	**Snohvit**
Country		Norway	Norway
Start		1996	2006
Storage type		Aquifer	Aquifer
Annual CO_2 injection rate	$MtCO_2$/year	1	0.7
Onshore/Offshore		Offshore	Offshore
Number of wells		1	1
Pipeline length	km	0	160
Capital Investment Costs			
Capture and Transport	**$ million**	**79**	**143**
Compression and dehydration	$ million	79	70
Pipeline	$ million	none	73
Storage	**$ million**	**15**	**48**
Drilling and well completion	$ million	15	25
Facilities	$ million	[a]	12
Other	$ million	[a]	11
Total capital investment costs	**$ million**	**94**	**191**
Operating Costs			
Fuel and CO_2 tax	$ million	7	
References		Torp and Brown, 2005	Kaarstad, 2002

[a] No further breakdown figures are available. Subset of a larger system of capital and operating costs for several processes, mostly natural gas and condensate processing.

Figures

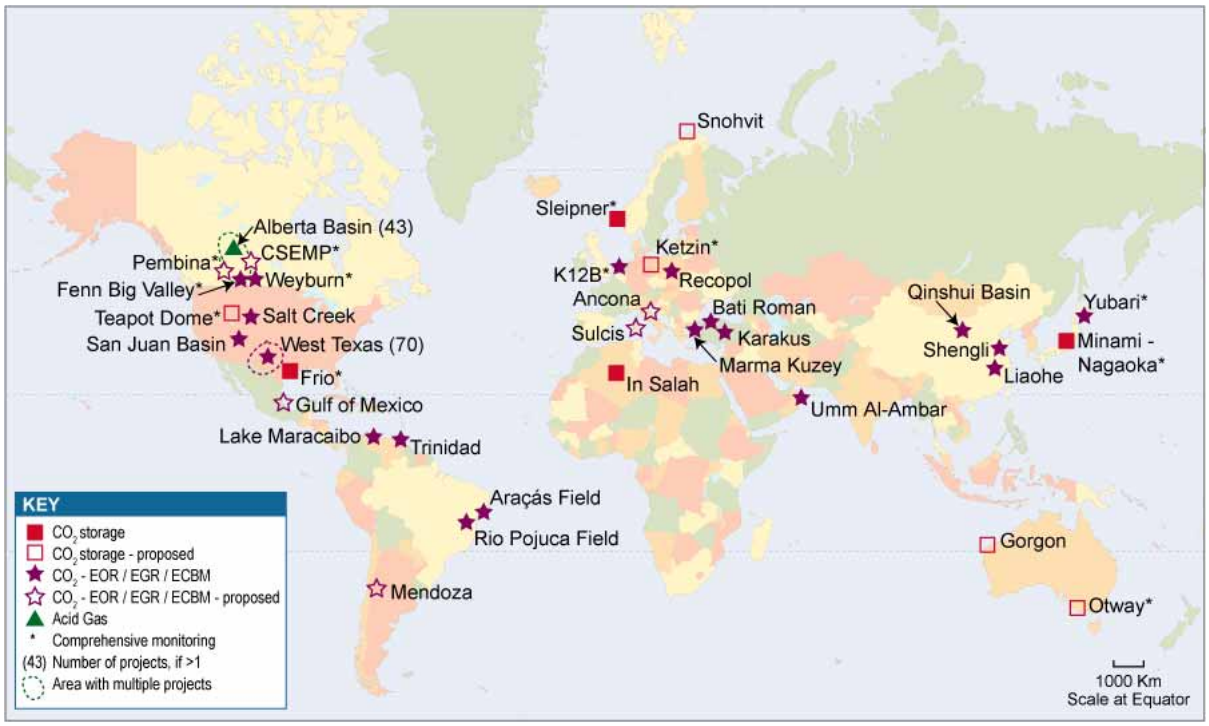

Figure 5.1. Location of sites where activities relevant to CO_2 storage are planned or under way.

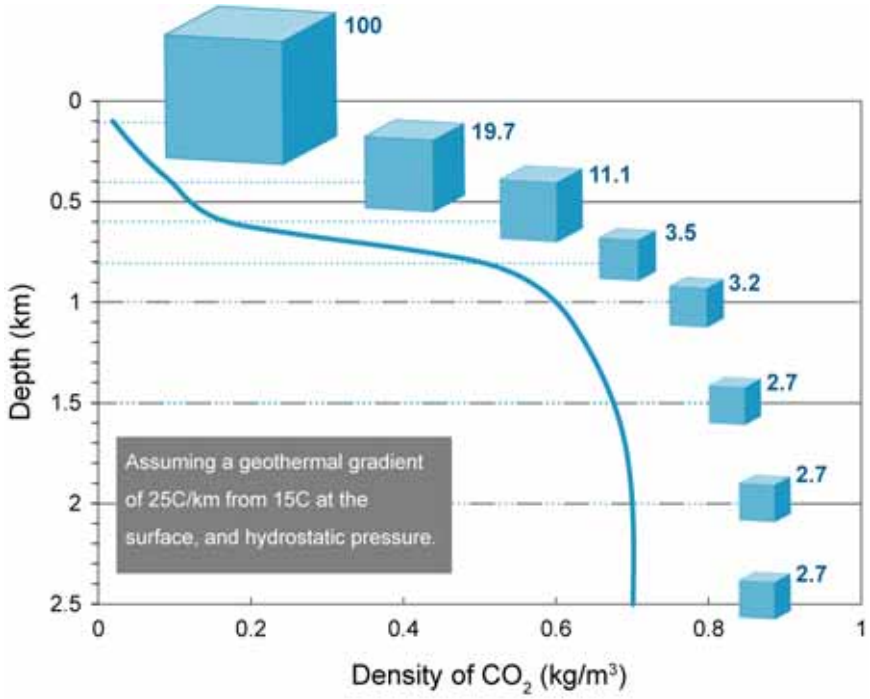

Figure 5.2. Variation of CO_2 density with depth, assuming hydrostatic pressure and a geothermal gradient of 25°C/km from 15°C at the surface (based on values from Angus et al., 1973). Carbon dioxide density increases rapidly at approximately 800 m depth, as the CO_2 reaches a supercritical state. Cubes are representative of the relative volume occupied by the CO_2, and up to 800 m, this volume can be seen to dramatically decrease with depth. At depths below1.5 km, the density and specific volume become nearly constant.

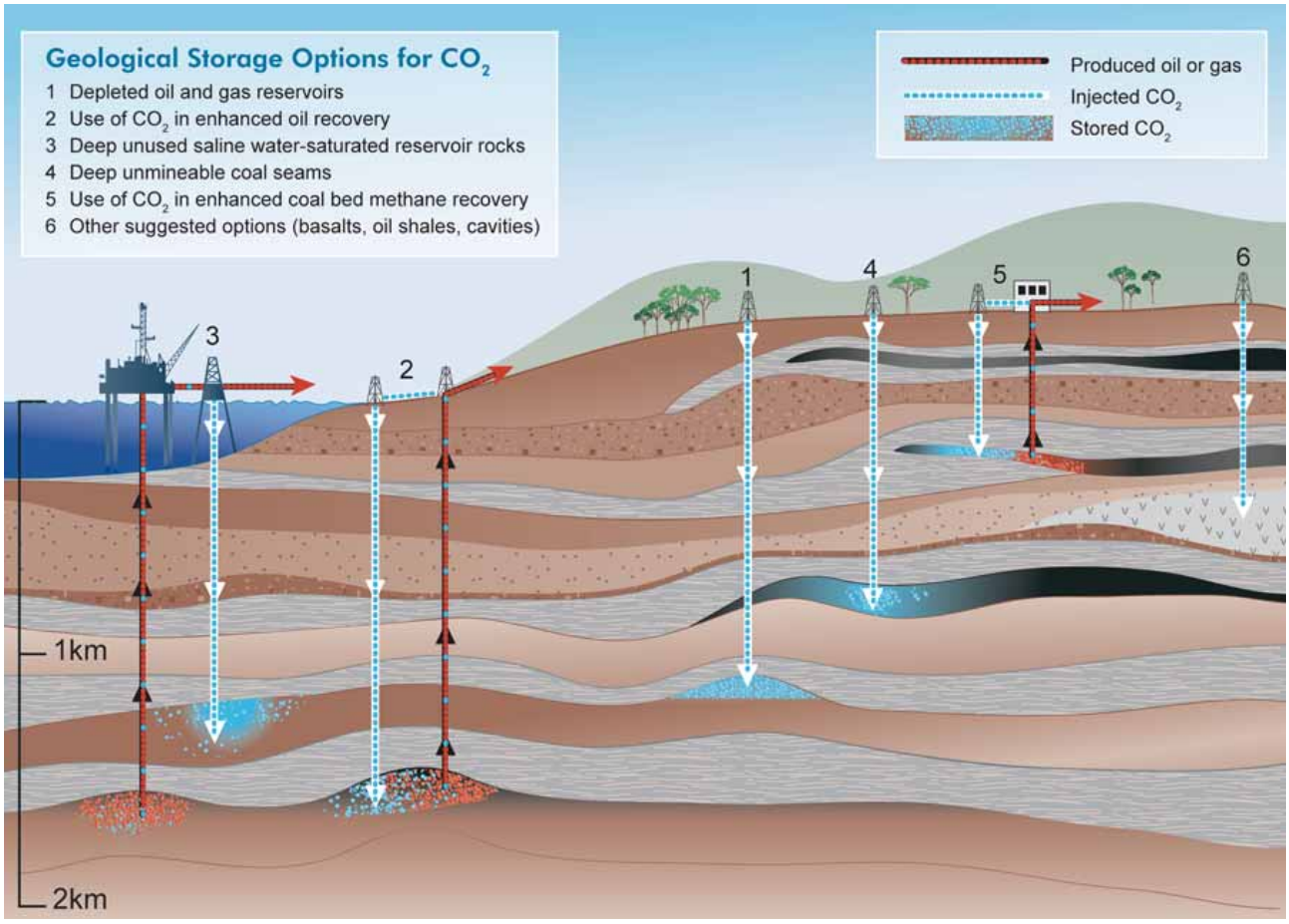

Figure 5.3. Options for storing CO_2 in deep underground geological formations (after Cook, 1999).

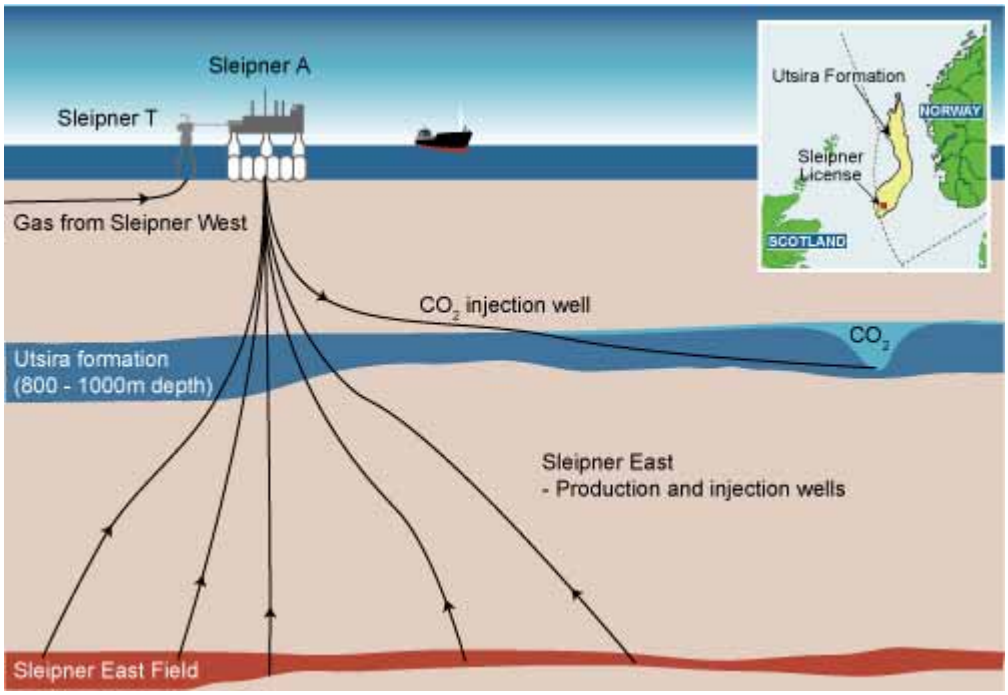

Figure 5.4. Simplified diagram of the Sleipner CO_2 Storage Project. Inset: location and extent of the Utsira formation.

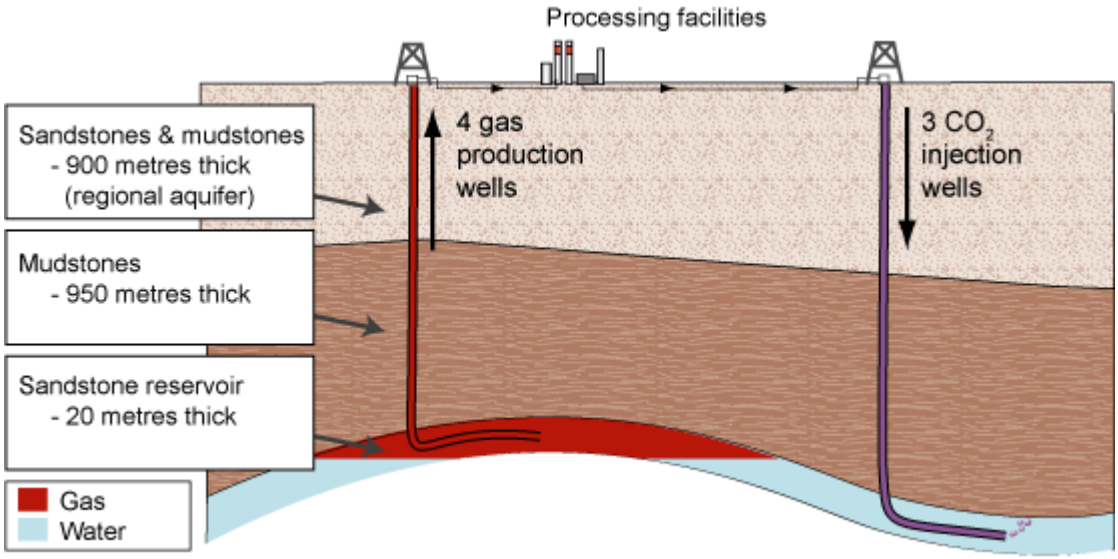

Figure 5.5. Schematic of the In Salah Gas Project, Algeria. One $MtCO_2$ will be stored annually in the gas reservoir. Long- reach horizontal wells with slotted intervals of up to 1.5 km are used to inject CO_2 into the water-filled parts of the gas reservoir.

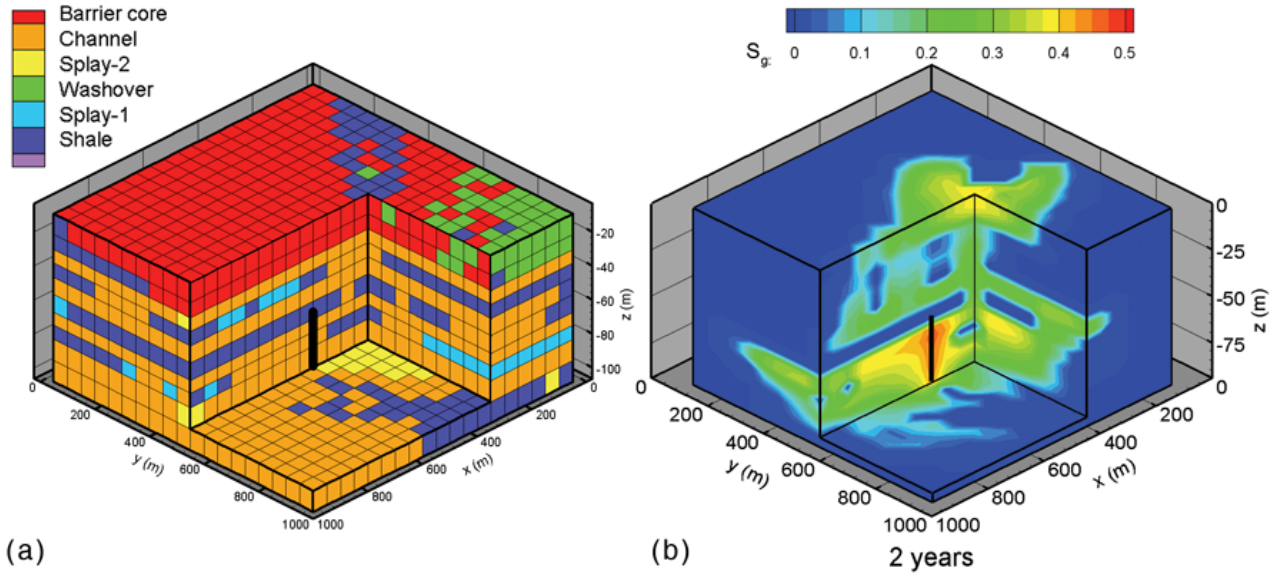

Figure 5.6. Simulated distribution of CO_2 injected into a heterogeneous formation with low permeability layers that block upwards migration of CO_2. (a) Illustration of a heterogeneous formation facies grid model. The location of the injection well is indicated by the line in the lower portion of the grid. (b) The CO_2 distribution after 2 years of injection. Note that the simulated distribution of CO_2 is strongly influenced by the low permeability layers. These block and delay upward movement of CO_2 (after Doughty and Pruess, 2004).

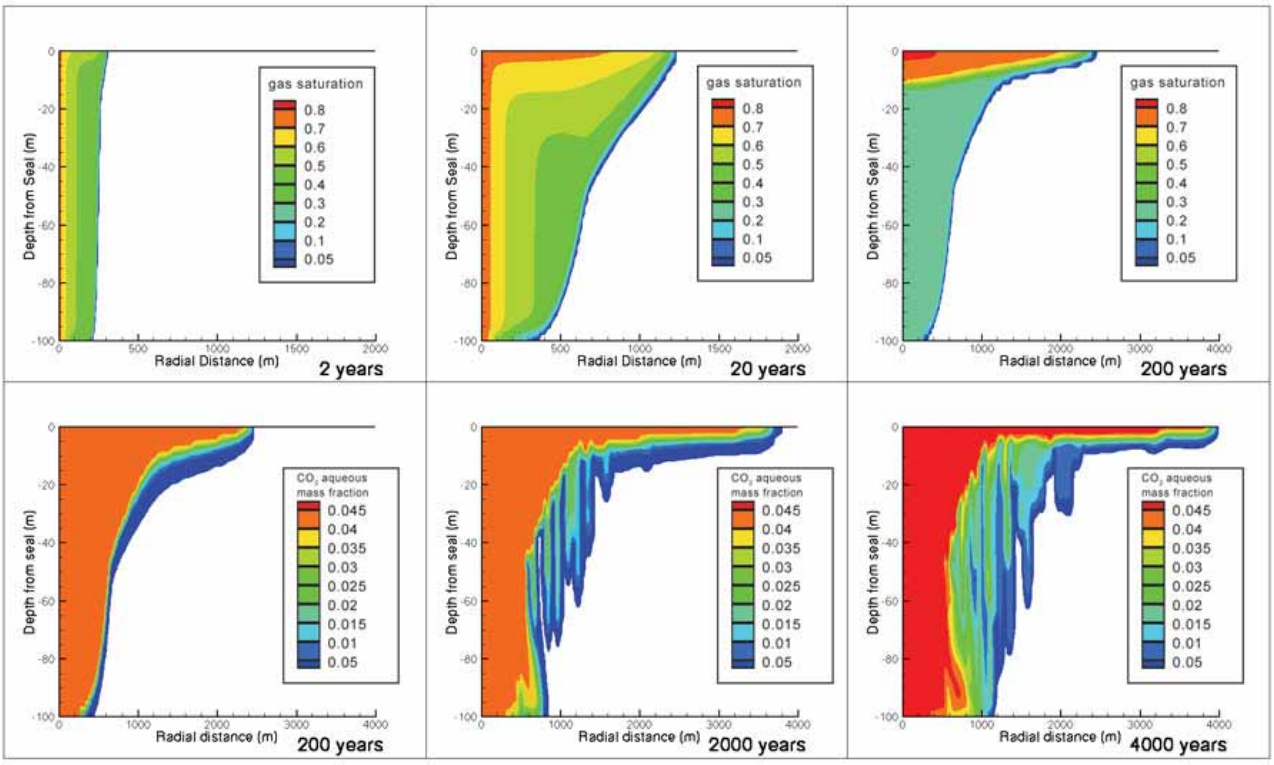

Figure 5.7. Radial simulations of CO_2 injection into a homogeneous formation 100m thick, at a depth of 1 km, where the pressure is 10 MPa and the temperature is 40 C. The injection rate is 1 $MtCO_2$ per year for 20 years, the horizontal permeability is $10^{(-13)}$ m^2 (approximately 100 mD), and the vertical permeability is one tenth of that. The residual CO_2 saturation is 20%. The first three parts of the Figure at 2, 20 and 200 years show the gas saturation in the porous medium, while the second three parts of the figure at 200, 2000 and 4000 years show the mass fraction of dissolved carbon dioxide in the aqueous phase. (after Ennis-King and Paterson, 2003).

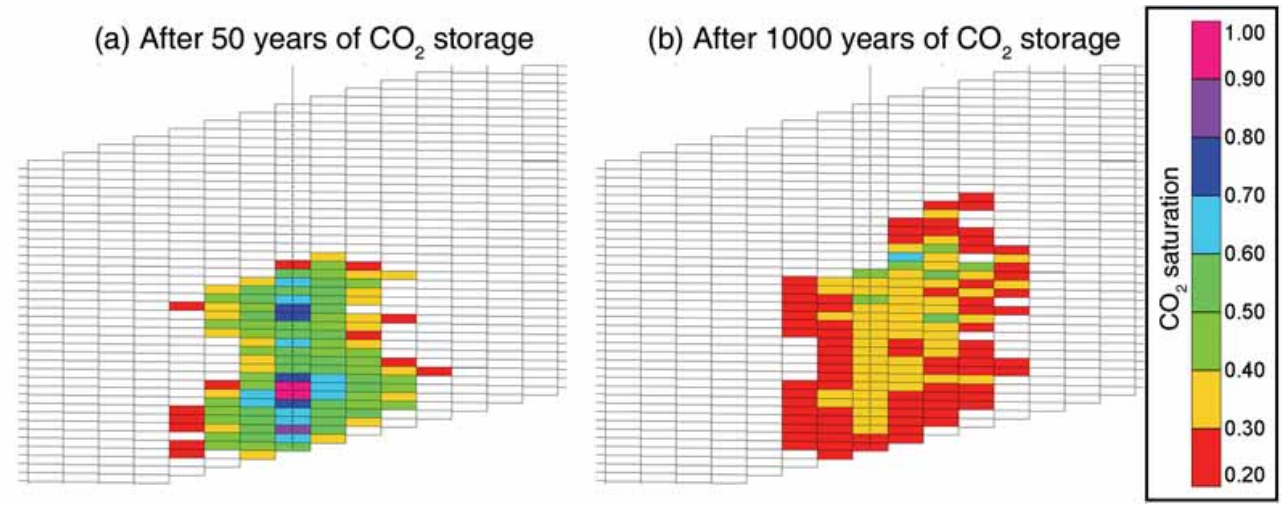

Figure 5.8. Simulation of 50 years of injection of CO_2 into the base of a saline aquifer, capillary forces trap CO_2 in the pore space of sedimentary rocks: (a) After 50-year injection period is over most CO_2 is still mobile, driven upwards by buoyancy forces; (b) After 1000 years, buoyancy-driven flow has expanded the volume affected by CO_2, and much is trapped as residual CO_2 saturation or dissolved in brine (not shown). Little CO_2 is mobile and all CO_2 is contained within the aquifer (after Kumar et al., 2004b).

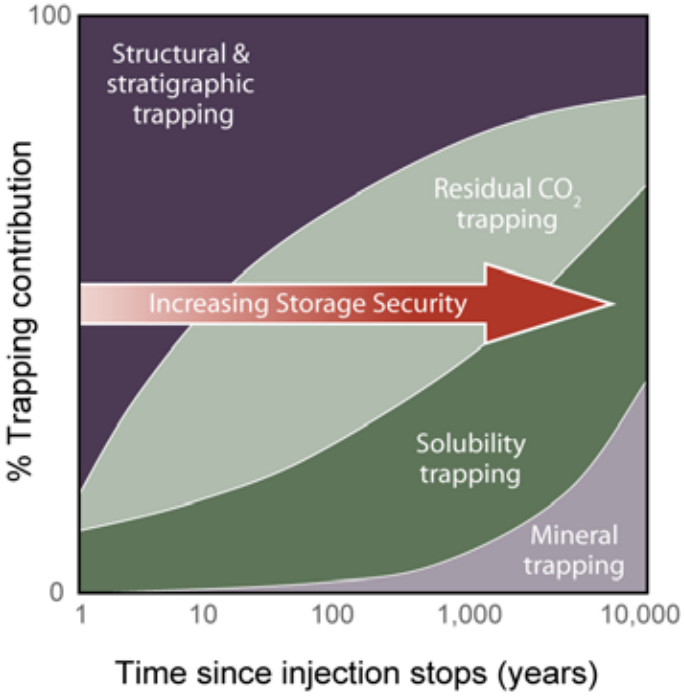

Figure 5.9. Storage security depends on a combination of physical and geochemical trapping. Over time, residual CO_2 trapping, solubility trapping and mineral trapping increase.

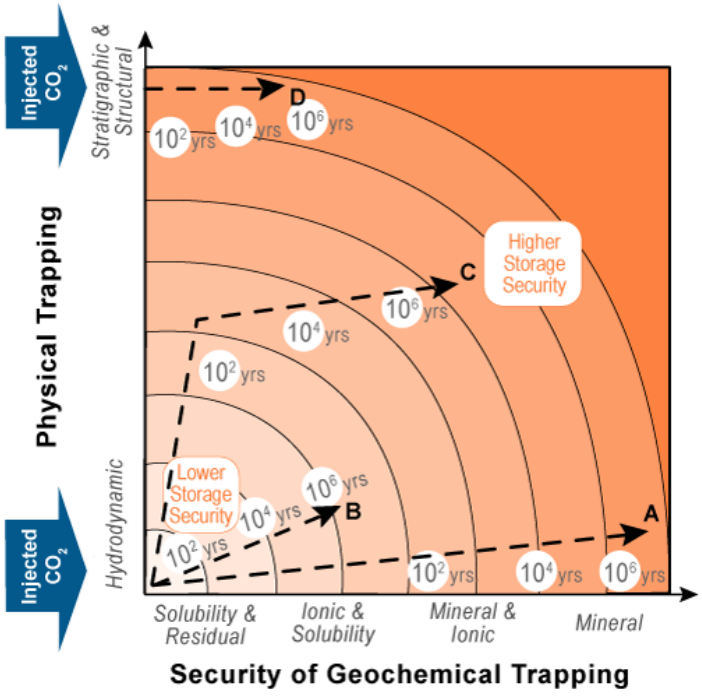

Figure 5.10. Storage expressed as a combination of physical and chemical trapping. Level of security is proportional to distance from origin. Dashed lines are examples of million year pathways, discussed in the text.

Figure 5.11. Examples of some natural accumulations of CO_2 around the world. Regions containing many occurrences are enclosed by a dashed line. Natural accumulations can be useful as analogues for certain aspects of storage and for assessing the environmental impacts of leakage. Data quality is variable and the apparent absence of accumulations in South America, southern Africa and central and northern Asia is probably more a reflection of lack of data than a lack of CO_2 accumulations.

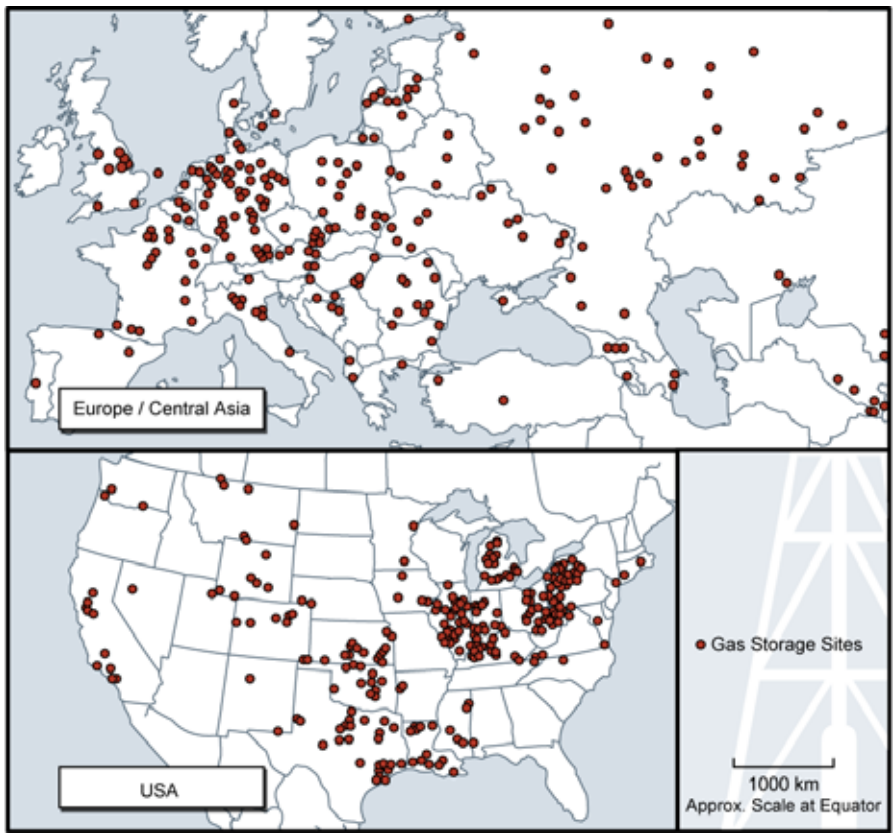

Figure 5.12. Location of some natural gas storage projects.

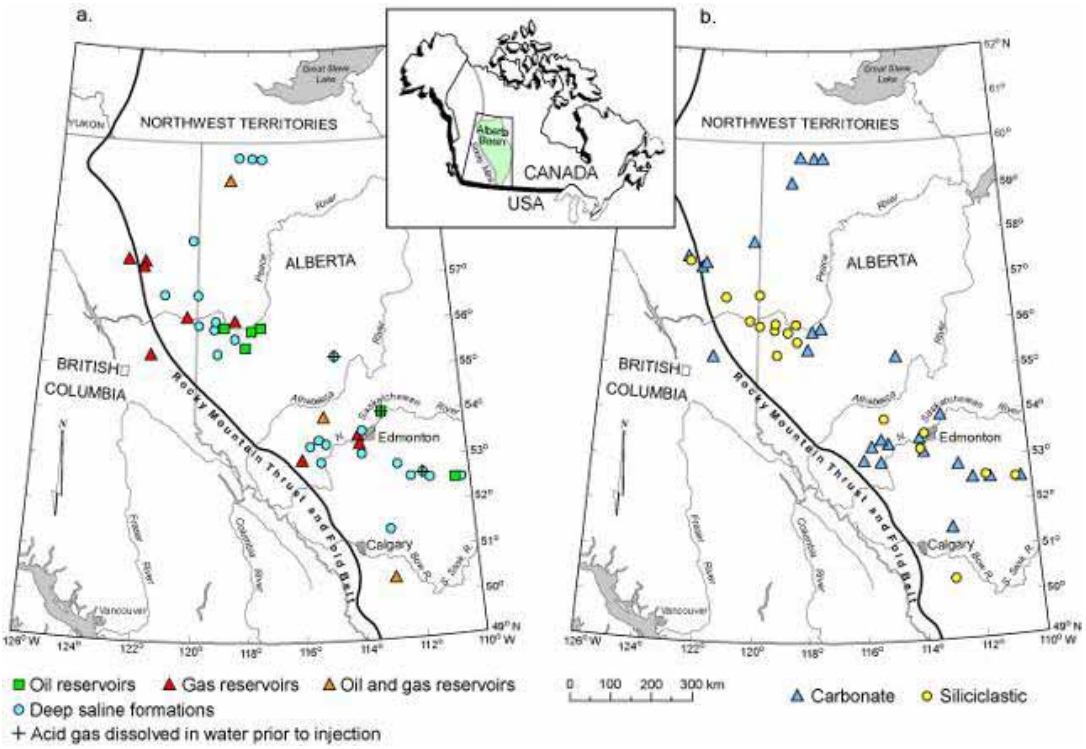

Figure 5.13. Locations of acid gas injection sites in the Alberta Basin, Canada: (a) classified by injection unit; (b) classified by rock type (from Bachu and Haug, 2005).

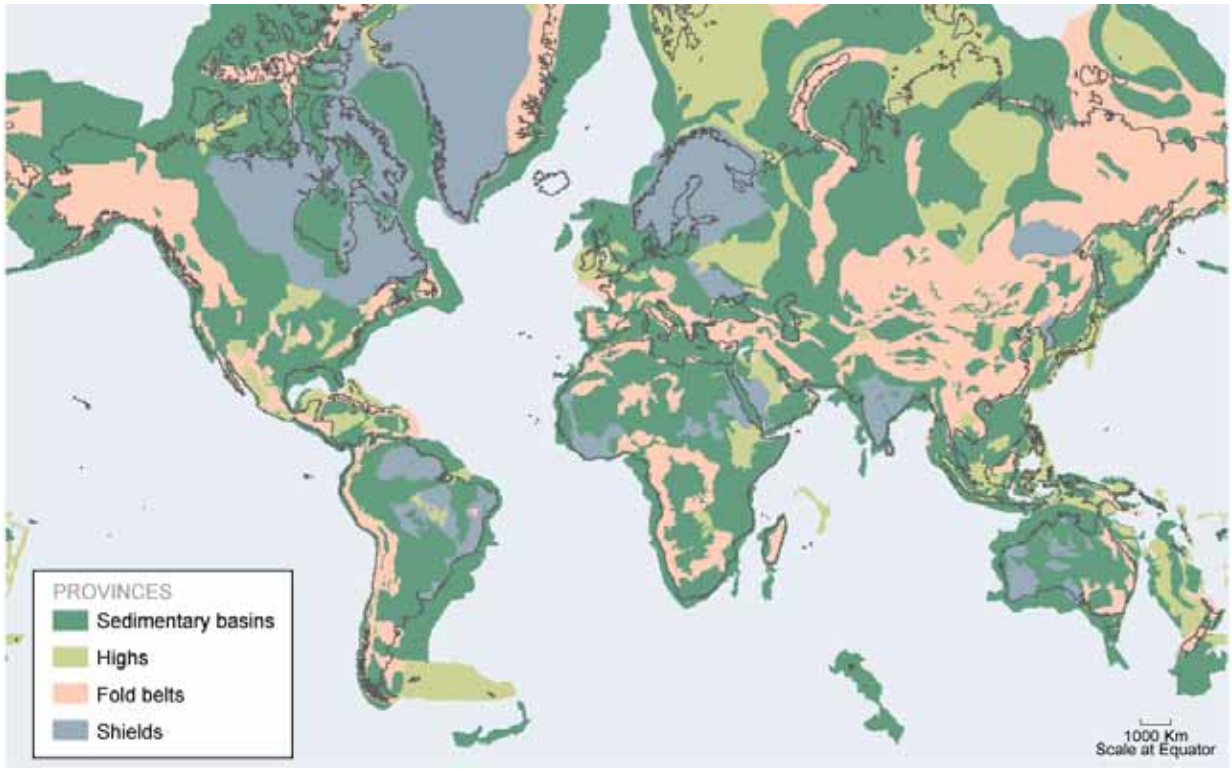

Figure 5.14. Distribution of sedimentary basins around the world (after Bradshaw and Dance, 2005, and USGS, 2001a). In general sedimentary basins are likely to be the most prospective areas for storage sites. However, storage sites may also be found in some areas of fold belts and in some of the highs. Shield areas constitute regions with low prospectivity for storage. The Mercator projection used here is to provide comparison with Figures 5.1, 5.8, and 5.23. The apparent

dimensions of the sedimentary basins, particularly in the northern hemisphere, should not necessarily be taken as an indication of their likely storage capacity.

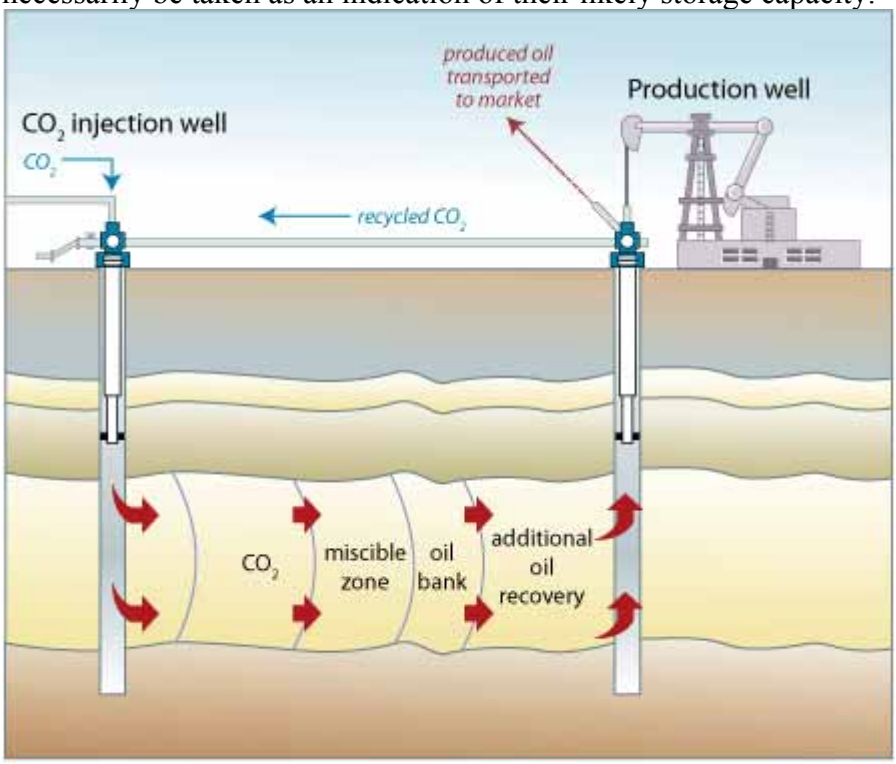

Figure 5.15. Injection of CO_2 for enhanced oil recovery (EOR) with some storage of retained CO_2 (after IEA Greenhouse Gas R&D Programme). The CO_2 that is produced with the oil is separated and reinjected back into the formation. Recycling of produced CO_2 decreases the amount of CO_2 that must be purchased and avoids emissions to the atmosphere.

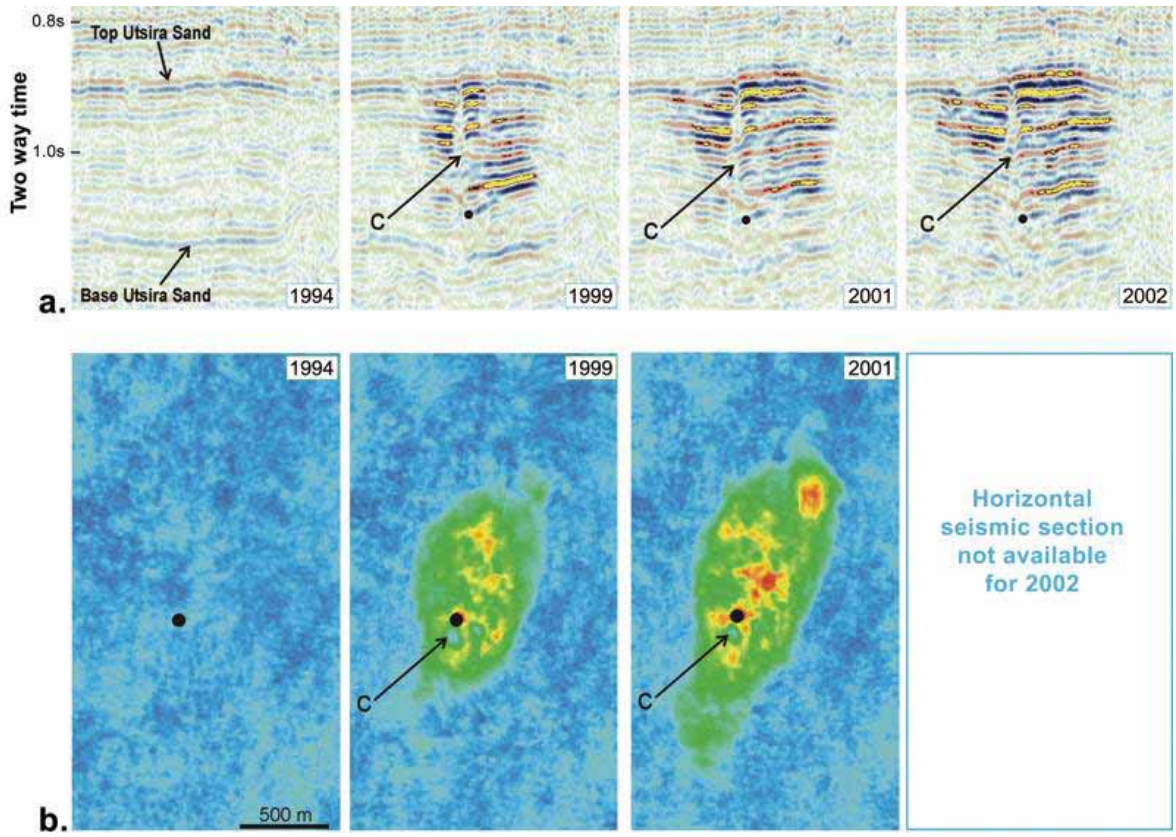

Figure 5.16. (a) Vertical seismic sections through the CO_2 plume in the Utsira Sand at the Sleipner gas field, North Sea, showing its development over time. Note the chimney of high CO_2 saturation (c) above the injection point (black dot) and the bright layers corresponding to high acoustic response due to CO_2 in a gas form being resident in sandstone beneath thin low-permeability horizons within the reservoir; (b) horizontal seismic sections through the developing CO_2 plume at Sleipner showing its growth over time, not available for 2002 because the CO_2 plume-specific monitoring was completed in 2001 (courtesy of Andy Chadwick and the CO2STORE project).

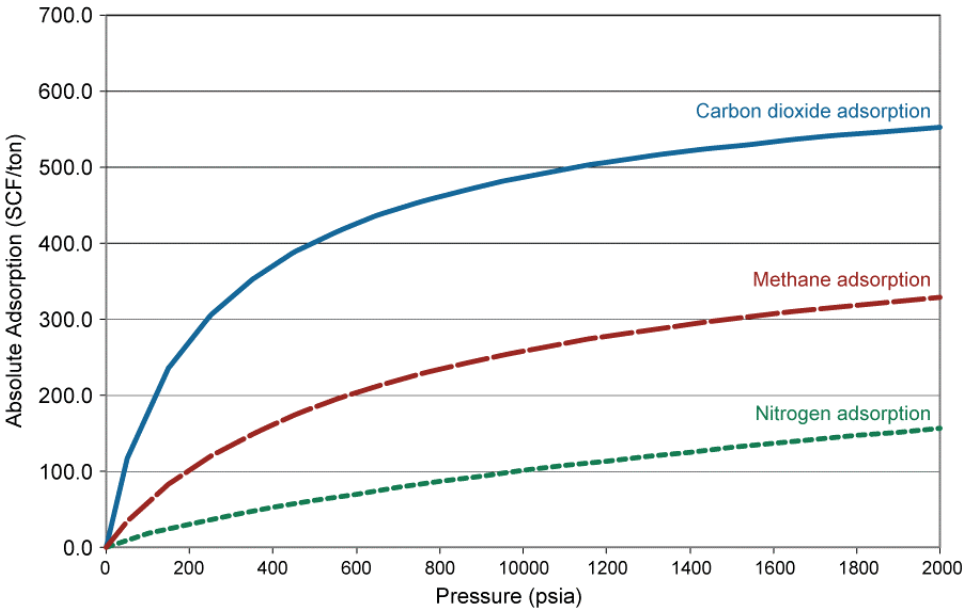

Figure 5.17. Pure gas absolute adsorption in standard cubic feet per tonne (SCF/tonne) on Tiffany Coals at 130°F (after Gasem et al., 2002).

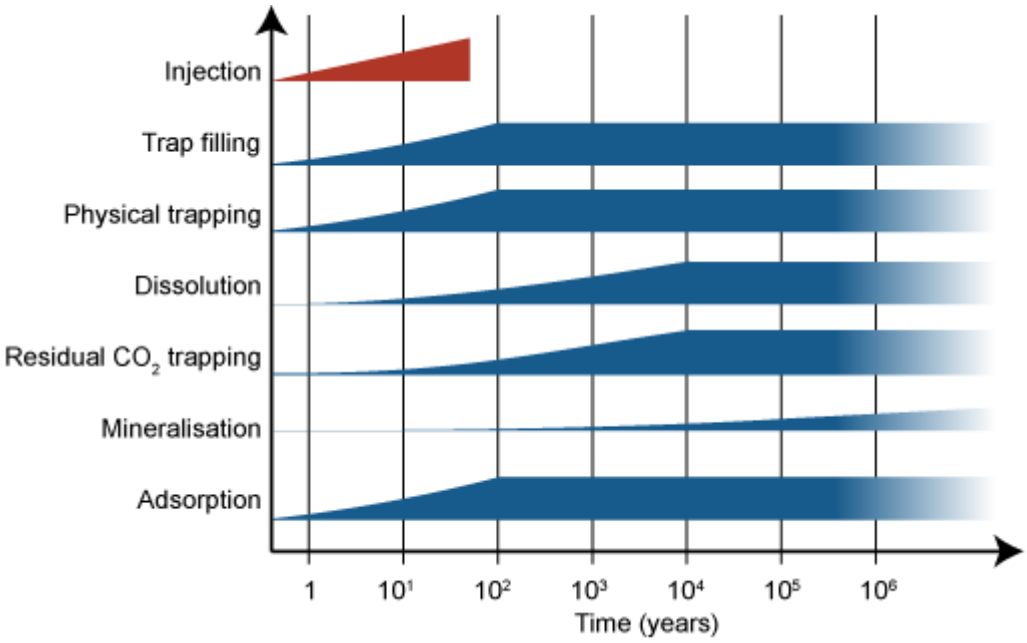

Figure 5.18. Schematic showing the time evolution of various CO_2 storage mechanisms operating in deep saline formations, during and following injection. Assessing storage capacity is complicated by the different time and spatial scales over which these processes occur.

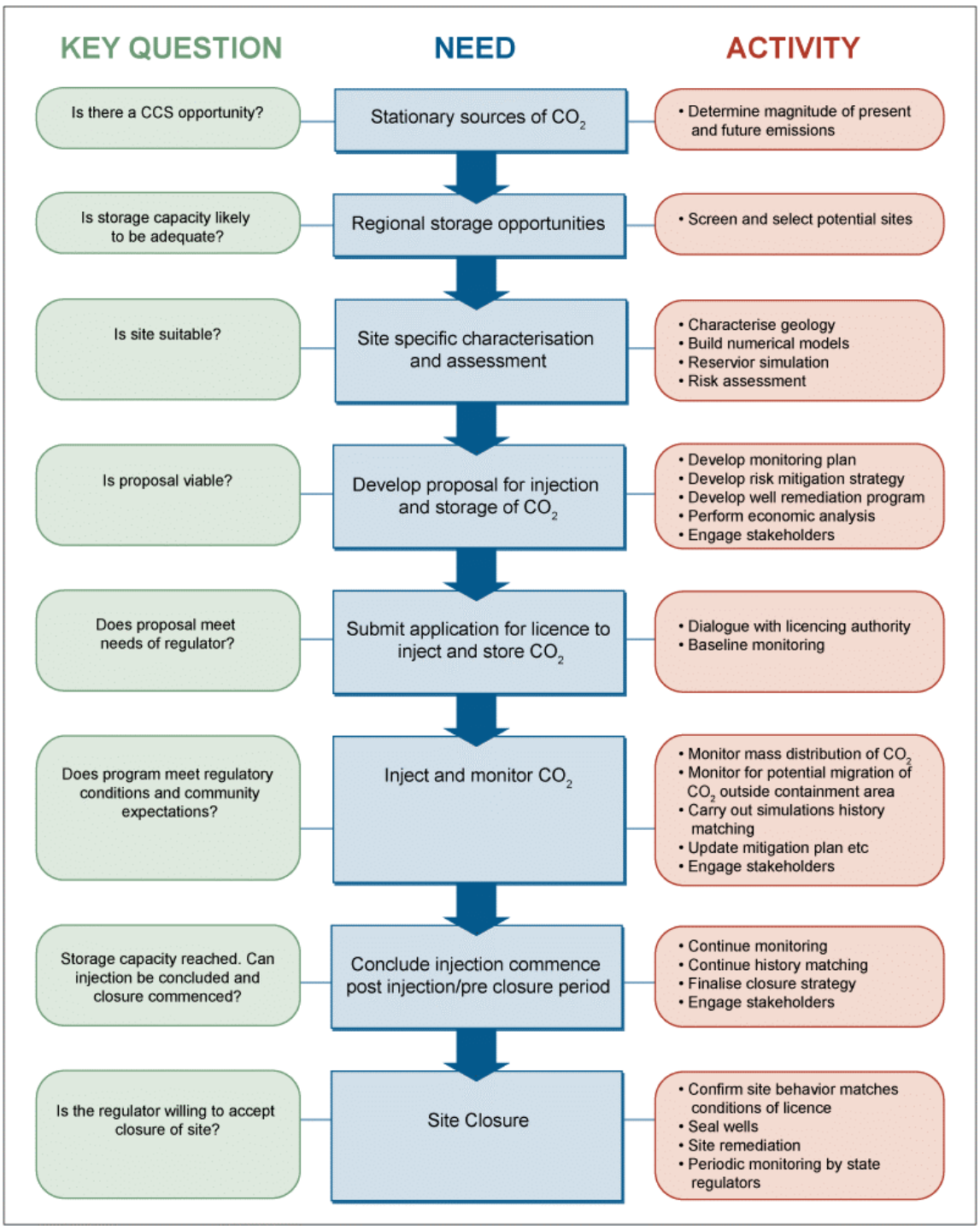

Figure 5.19. Life cycle of a CO_2 storage project showing the importance of integrating site characterisation with a range of regulatory, monitoring, economic, risking and engineering issues.

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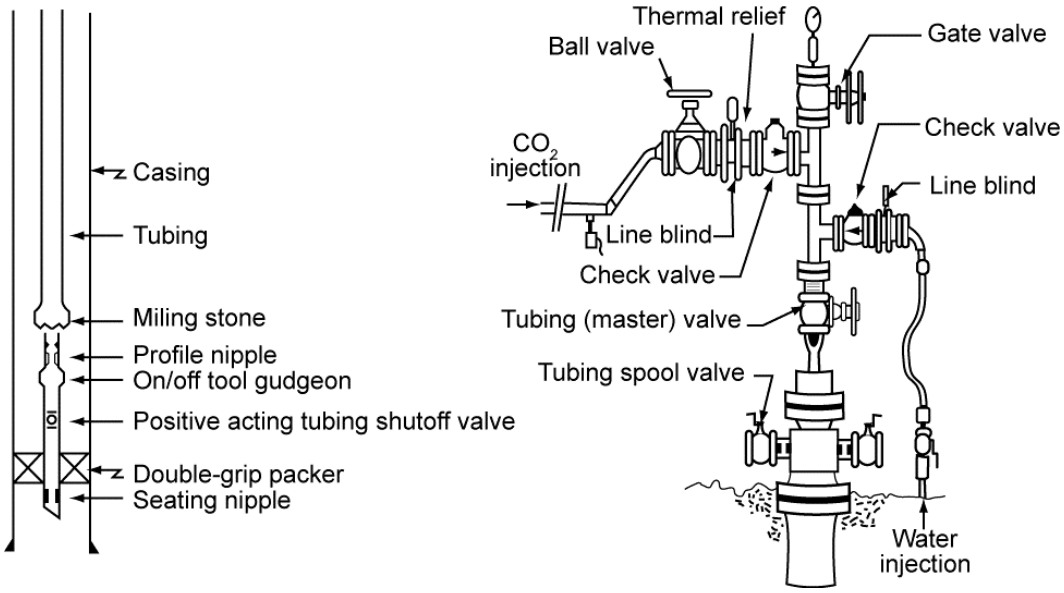

Figure 5.20. Typical CO_2 injection well and wellhead configuration.

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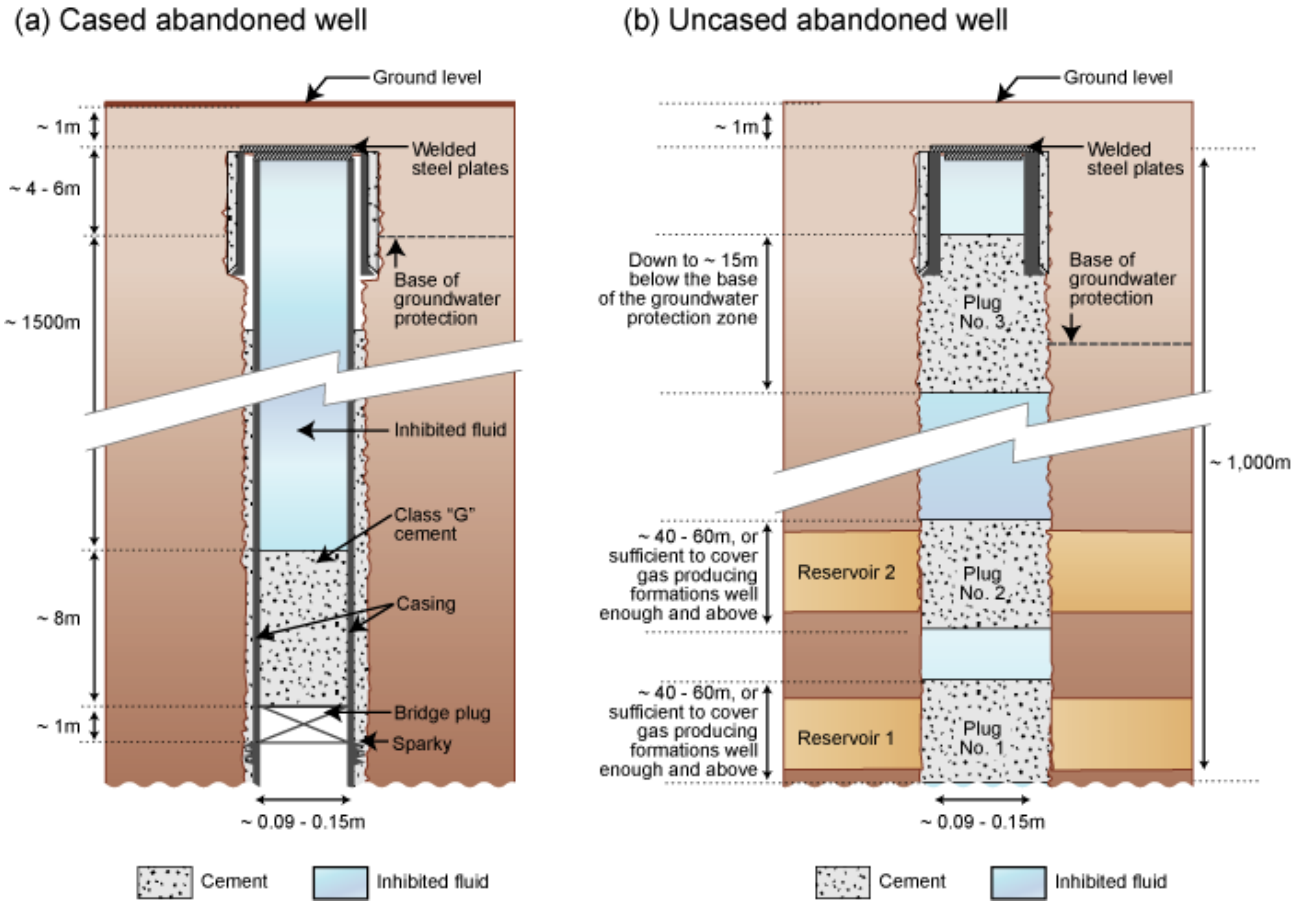

Figure 5.21. Examples of how cased and uncased wells are abandoned today. Special requirements
10 may be developed for abandoning CO_2 storage wells, including use of corrosion resistant cement plugs and removing all or part of the casing in the injection interval and caprock.

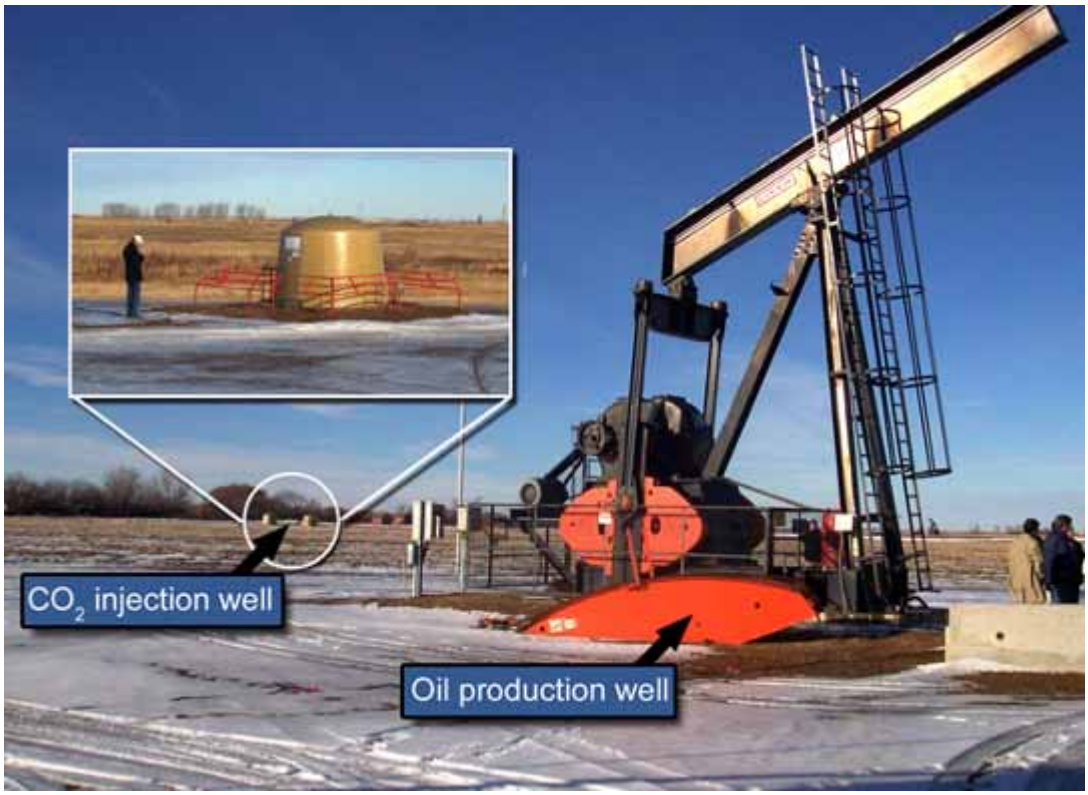

Figure 5.22. Typical CO_2 field operation set up: Weyburn surface facilities.

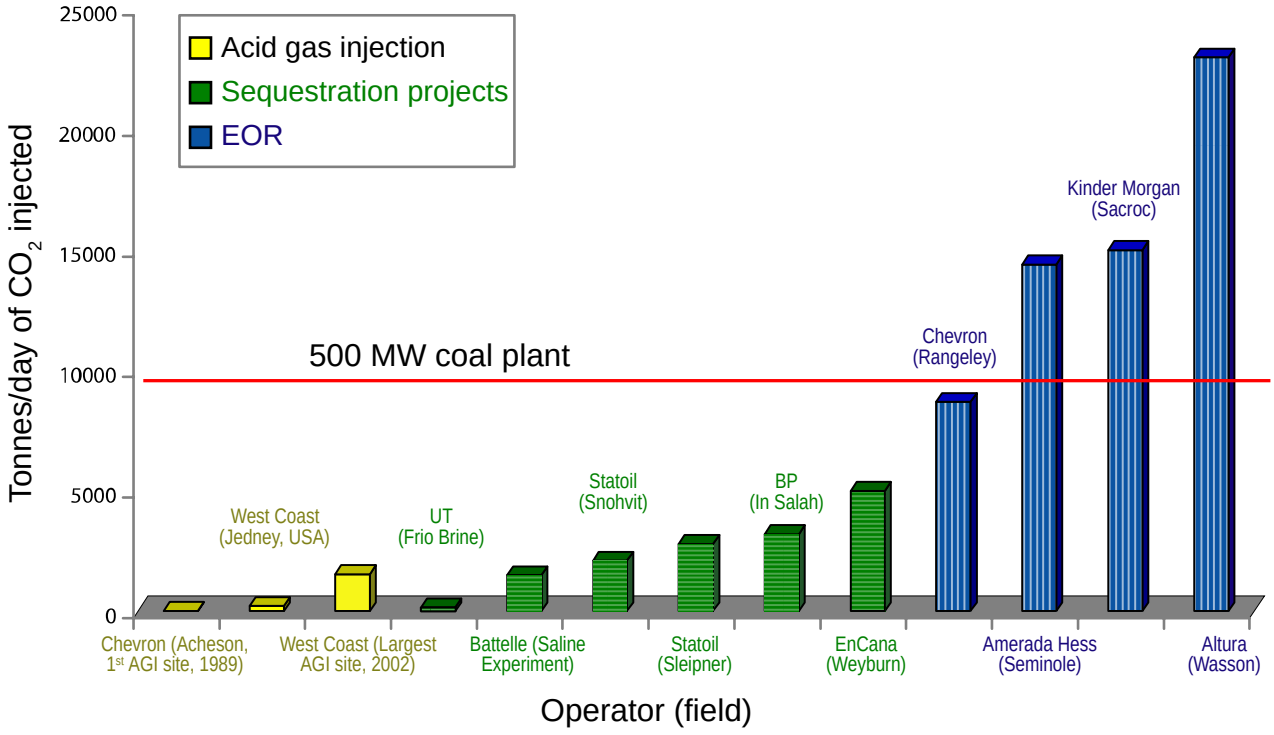

Figure 5.23. Comparison of the magnitude of CO_2 injection activities illustrating that the storage operations from a typical 500 MW coal plant will be on the same order of magnitude as existing CO_2 injection operations (after Heinrich et al., 2003).

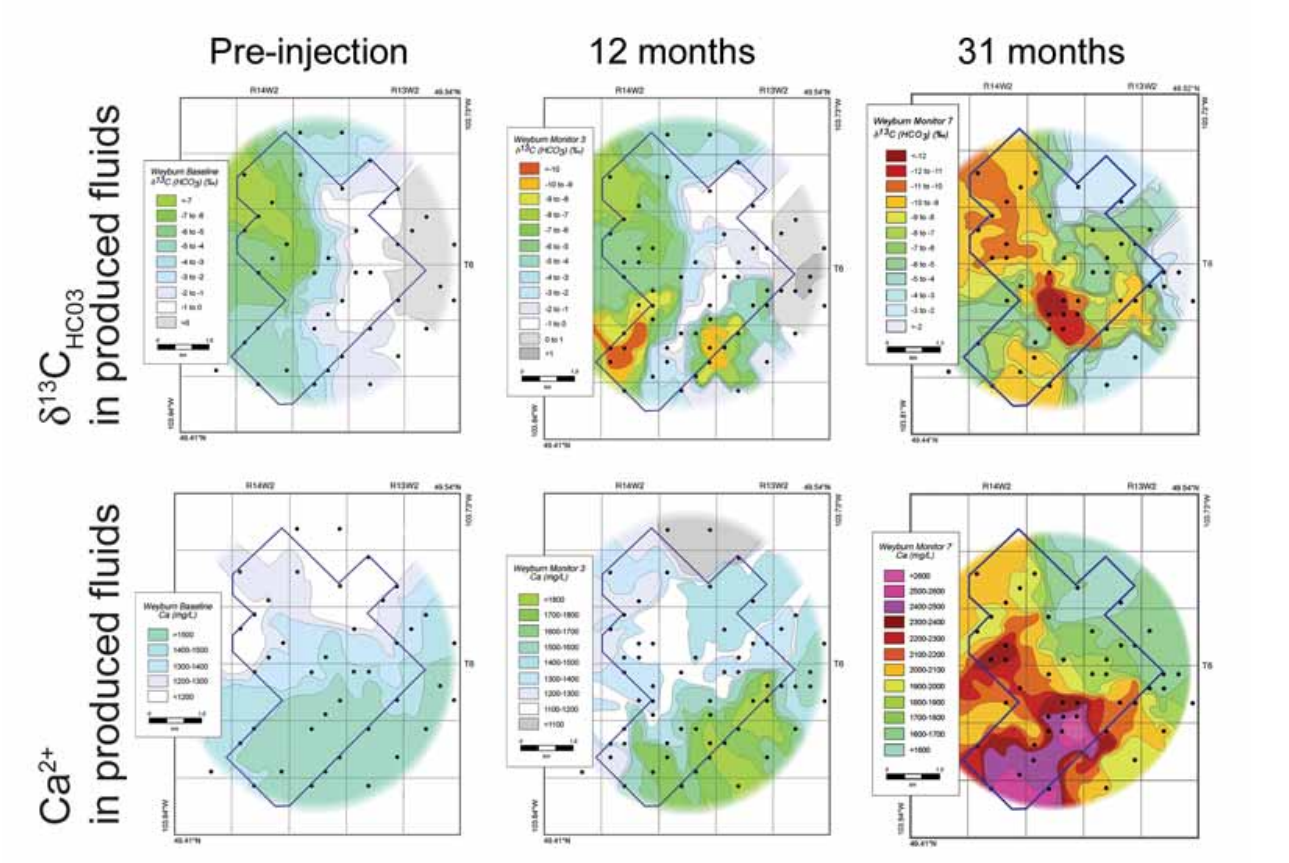

Figure 5.24. The produced water chemistry prior to CO_2 injection, and the produced water chemistry after 12 months and 36 months of injection at Weyburn has been contoured based on fluid samples taken at various production wells. The black dots show the location of the sample wells: (a) $\delta^{13}C_{HCO3}$ in the produced water, showing the effect of supercritical CO_2 dissolution and mineral reaction; (b) Calcium concentrations in the produced water showing the result of mineral dissolution (after Perkins et al., 2005).

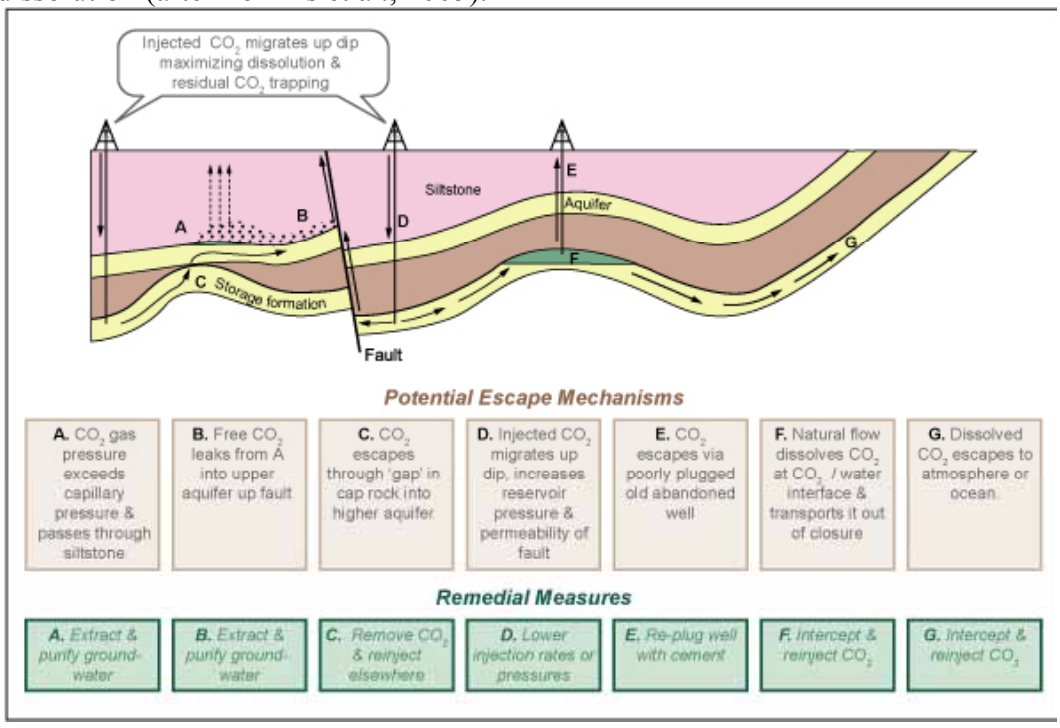

Figure 5.25. Some potential escape routes for CO_2 injected into saline formations.

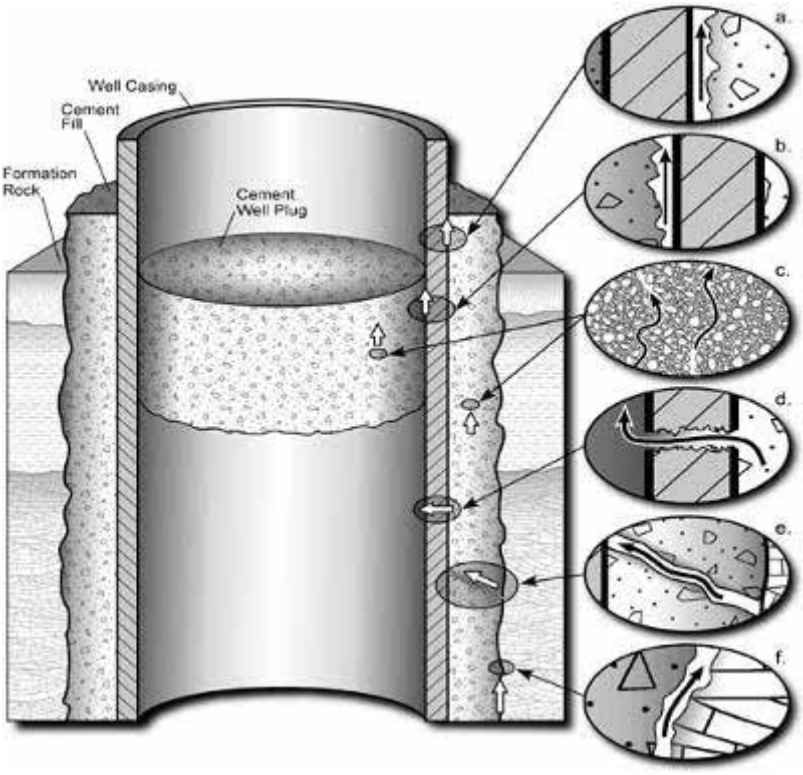

Figure 5.26. Possible leakage pathways in an abandoned well: (a) and (b) between casing and cement wall and plug, respectively; (c) through cement plugs; (d) through casing; (e) through cement wall; and (f) between the cement wall and rock (after Gasda et al., 2004).

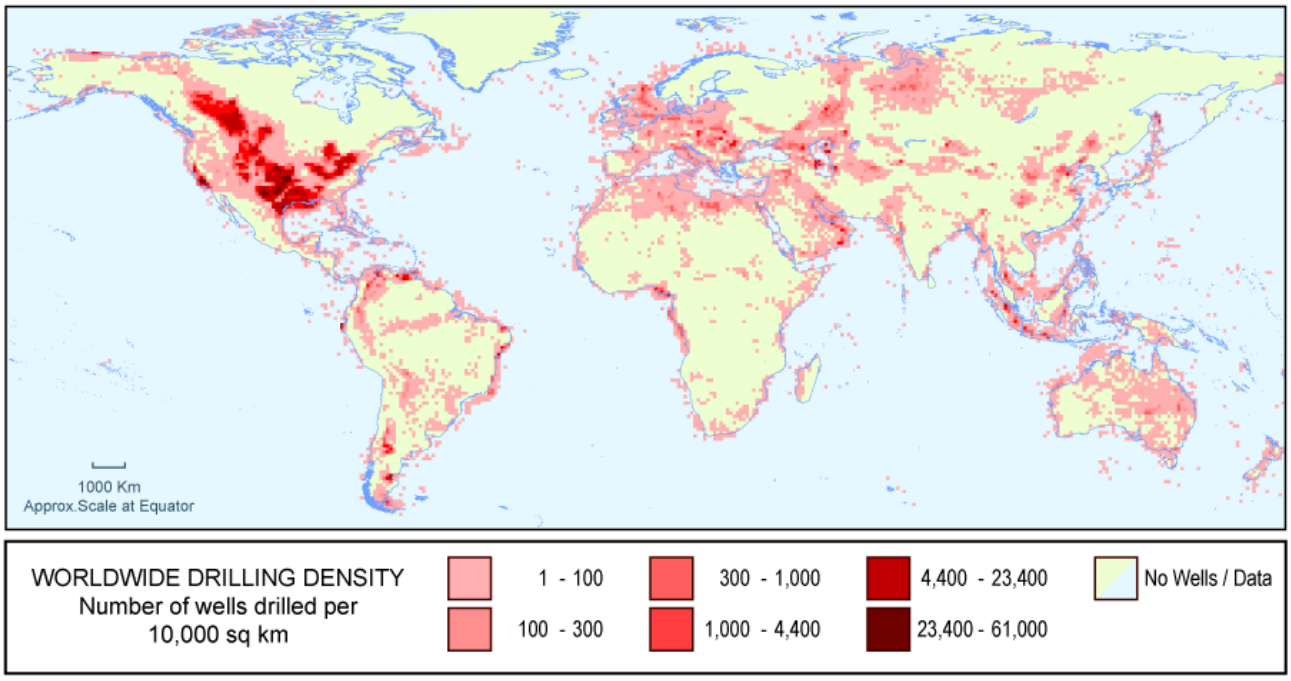

Figure 5.27. World oil and gas well distribution and density (courtesy of IHS Energy).

6. Ocean storage

Coordinating Lead Authors

KEN CALDEIRA (UNITED STATES), MAKOTO AKAI (JAPAN)

Lead Authors

Peter Brewer (United States), Baixin Chen (China), Peter Haugan (Norway), Toru Iwama (Japan), Paul Johnston (United Kingdom), Haroon Kheshgi (United States), Qingquan Li (China), Takashi Ohsumi (Japan), Hans Pörtner (Germany), Chris Sabine (United States), Yoshihisa Shirayama (Japan), Jolyon Thomson (United Kingdom)

Contributing Authors

Jim Barry (United States), Lara Hansen (United States)

Review Editors

Brad De Young (Canada), Fortunat Joos (Switzerland)

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Executive Summary

Captured CO_2 could be deliberately injected into the ocean at great depth, where most of it would remain isolated from the atmosphere for centuries. CO_2 can be transported via pipeline or ship for release in the ocean or on the sea floor. There have been small-scale field experiments and 25 years of theoretical, laboratory, and modelling studies of intentional ocean storage of CO_2, but ocean storage has not yet been deployed or thoroughly tested.

The increase in atmospheric CO_2 concentrations due to anthropogenic emissions has resulted in the oceans taking up CO_2 at a rate of about 7 $GtCO_2$ yr^{-1} (2 GtC yr^{-1}). Over the past 200 years the oceans have taken up 500 $GtCO_2$ from the atmosphere out of 1300 $GtCO_2$ total anthropogenic emissions. Anthropogenic CO_2 resides primarily in the upper ocean and has thus far resulted in a decrease of *p*H of about 0.1 at the ocean surface with virtually no change in *p*H deep in the oceans. Models predict that the oceans will take up most CO_2 released to the atmosphere over several centuries as CO_2 is dissolved at the ocean surface and mixed with deep ocean waters.

The Earth's oceans cover over 70% of the Earth's surface with an average depth of ~3800 meters; hence, there is no practical physical limit on the amount of anthropogenic CO_2 that could be placed in the ocean. However, the amount that is stored in the ocean on the millennial time scale depends on oceanic equilibration with the atmosphere. Over millennia, CO_2 injected into the oceans at great depth will approach approximately the same equilibrium as if it were released to the atmosphere. Sustained atmospheric CO_2 concentrations in the range of 350 to 1000 ppm imply that 2300 ± 260 to 10,700 ± 1000 Gt of anthropogenic CO_2 will eventually reside in the ocean.

Analyses of ocean observations and models agree that injected CO_2 will be isolated from the atmosphere for several hundred years and that the fraction retained tends to be larger with deeper injection. Additional concepts to prolong CO_2 retention include forming solid CO_2 hydrates and liquid CO_2 lakes on the sea floor, and increasing CO_2 solubility by, for example, dissolving mineral carbonates. Over centuries, ocean mixing results in loss of isolation of injected CO_2, and exchange with the atmosphere, that would be gradual from large regions of the ocean. There are no known mechanisms for sudden or catastrophic release of injected CO_2.

Injection up to a few $GtCO_2$ would produce a measurable change in ocean chemistry in the region of injection, whereas injection of hundreds of $GtCO_2$ would eventually produce measurable change over the entire ocean volume.

Experiments show that added CO_2 can harm marine organisms. Effects of elevated CO_2 levels have mostly been studied on time scales up to several months in individual organisms that live near the ocean surface. Observed phenomena include reduced rates of calcification, reproduction, growth, circulatory oxygen supply and mobility as well as increased mortality over time. In some organisms these effects are seen in response to small additions of CO_2. Immediate mortality is expected close to injection points or CO_2 lakes. Chronic effects may set in with small degrees of long-term CO_2 accumulation, such as might result far from an injection site, however, long-term chronic effects have not been studied in deep-sea organisms.

CO_2 effects on marine organisms will have ecosystem consequences; however, no controlled ecosystem experiments have been performed in the deep ocean. Thus, only a preliminary assessment of potential ecosystem effects can be given. It is expected that ecosystem consequences will increase with increasing CO_2 concentration, but no environmental thresholds have been

identified. It is also presently unclear, how species and ecosystems would adapt to sustained, elevated CO_2 levels.

Chemical and biological monitoring of an injection project, including observations of the spatial and temporal evolution of the resulting CO_2 plume, would help evaluate the amount of materials released, the retaining of CO_2, and some of the potential environmental effects.

For water column and sea floor release, capture and compression/liquefaction are thought to be the dominant cost factors. Transportation (i.e., piping, and shipping) costs are expected to be the next largest cost component and scale with proximity to the deep ocean. The costs of monitoring, injection nozzles etc. are expected to be small in comparison.

Dissolving mineral carbonates, if found practical, could increase the fraction retained for stored carbon dioxide to ~10^4 yr, minimize changes in ocean *p*H and CO_2 partial pressure, and may avoid the need for prior separation of CO_2. Large amounts of limestone and materials handling would be required for this approach.

Several different global and regional treaties on the law of the sea and marine environment could be relevant to intentional release of CO_2 into the ocean but the legal status of intentional carbon storage in the ocean has not yet been adjudicated.

It is not known whether the public will accept the deliberate storage of CO_2 in the ocean as part of a climate change mitigation strategy. Deep-ocean storage could help reduce the impact of CO_2 emissions on surface ocean biology but at the expense of effects on deep ocean biology.

6.1. Introduction and background

6.1.1 Intentional storage of CO_2 in the ocean

This report assesses what is known about intentional storage of carbon dioxide in the ocean by inorganic strategies that could be applied at industrial scale. Various technologies have been envisioned to enable and increase ocean CO_2 storage (Figure 6.1). One class of options involves storing a relatively pure stream of carbon dioxide that has been captured and compressed. This CO_2 can be placed on a ship, injected directly into the ocean, or deposited on the sea floor. CO_2 loaded on ships could either be dispersed from a towed pipe or transported to fixed platforms feeding a CO_2 lake on the sea floor. Such CO_2 lakes must be deeper than 3 km where CO_2 is denser than seawater. Any of these approaches could in principle be used in conjunction with neutralization with carbonate minerals.

Figure 6.1. Illustration of some of the ocean storage strategies described in this Chapter (figure courtesy Seán Goddard).

Research, development and analysis of ocean CO_2 storage concepts has progressed to consider key questions and issues that could affect the prospects of ocean storage as a response option to climate change (Section 6.2). Accumulated understanding of the ocean carbon cycle is being used to estimate how long CO_2 released into the oceans will remain isolated from the atmosphere; such estimates are used to assess the effectiveness of ocean storage concepts (Section 6.3).

Numerical model of the ocean indicate that placing CO_2 in the deep ocean would isolate most of the CO_2 from the atmosphere for several centuries, but over longer times the ocean and atmosphere

would equilibrate. Relative to atmospheric release, direct injection of CO_2 in to the ocean could reduce maximum amounts and rates of atmospheric CO_2 increase over the next several centuries (Figure 6.2; Kheshgi *et al.,* 1994; Kheshgi, 2004b). Direct injection of CO_2 in the ocean would not reduce atmospheric CO_2 content on the millennial time scale (Table 6.1; Figure 6.3; Hoffert *et al.*, 1979; Kheshgi *et al.*, 1994).

Table 6.1. Amount of additional CO_2 residing in the ocean after atmosphere-ocean equilibration for different atmospheric stabilization concentrations. Uncertainty range represents influence of climate sensitivity to a CO_2 doubling in the range of 1.5 K to 4.5 K (Kheshgi et al., 2005; Kheshgi 2004a). This table considers the possibility of increased carbon dioxide storage in the terrestrial biosphere; such an increase, if permanent, would allow a corresponding increase in total cumulative emissions. This table does not consider natural or engineered dissolution of carbonate minerals, which would increase ocean storage of anthropogenic carbon. Amount already in ocean exceeds 500 $GtCO_2$ (= 440 $GtCO_2$ for 1994 (Sabine et al., 2004) plus CO_2 absorption since that time). The long-term amount of CO_2 stored in the deep ocean is independent of whether the CO_2 is initially released to the atmosphere or the deep ocean.

Figure 6.2. Simulated atmospheric CO_2 resulting from CO_2 release to the atmosphere or injection into the ocean at 3,000 m depth (Kheshgi and Archer, 2004). Emissions follow a logistic trajectory with cumulative emissions of 18,000 $GtCO_2$. Illustrative cases include 100% of emissions released to the atmosphere leading to a peak in concentration, 100% of emissions injected into the ocean, and no emissions (e.g. permanent storage). Additional cases include 50% of emissions after 2050 either injected into the ocean (50% to atmosphere and 50% to ocean after 2050) or permanently sequestered stored (50% to atmosphere after 2050) with emissions prior to 2050 released to the atmosphere. Ocean injection results in lower peak concentrations in these cases. Over millennia, ocean injection cases approach that of atmospheric release. Simulated CO_2 then continues a downward trend due to modelled sediment dissolution.

Figure 6.3. Equilibrium partitioning of CO_2 between the ocean and atmosphere. On the time scale of millennia, complete mixing of the oceans leads to a partitioning of cumulative CO_2 emissions between the oceans and atmosphere with the bulk of emissions eventually residing in the oceans as dissolved inorganic carbon. The ocean partition depends non-linearly on CO_2 concentration according to carbonate chemical equilibrium (Box 6.1) and has limited sensitivity to changes in surface water temperature (shown be the grey area for a range of climate sensitivity of 1.5 to 4.5 C for CO_2 doubling) (adapted from Kheshgi et al., 2005; Kheshgi, 2004a). ΔpH evaluated from pCO_2 of 275 ppm. This calculation is relevant on the time scale of several centuries, and does not consider changes in ocean alkalinity that increase ocean CO_2 uptake over several millennia (Archer et al., 1997).

There has been limited experience with handling CO_2 in the deep-sea that could form a basis for the development of ocean CO_2 storage technologies. Before they could be deployed, such technologies would require further development and field testing. Associated with the limited level of development, estimates of the costs of ocean CO_2 storage technologies are at a primitive state, however, the costs of the actual dispersal technologies are expected to be low in comparison to the costs of CO_2 capture and transport to the deep-sea (but still non-negligible; Section 6.9). Proximity to the deep-sea is a factor, as the deep oceans are remote to many sources of CO_2 (Section 6.4). Ocean storage would require CO_2 transport by ship or deep-sea pipelines. Pipelines and drilling platforms, especially in oil and gas applications, are reaching ever-greater depths yet not on the scale or to the depth relevant for ocean CO_2 storage (Chapter 4). No insurmountable technical barrier to storage of CO_2 in the oceans is apparent.

Putting CO_2 directly into the deep ocean means that the chemical environment of the deep ocean would be altered immediately, and in concepts where release is from a point, change in ocean chemistry would be greater proximate to the release location. Given only rudimentary understanding of deep-sea ecosystems, only a limited and preliminary assessment of potential ecosystem effects can be given (Section 6.7).

Technologies exist to monitor deep-sea activities (Section 6.6). Practices for monitoring and verification of ocean storage would depend on which, as of yet undeveloped, ocean storage technology would potentially be deployed, and on environmental impacts to be avoided.

More carbon dioxide could be stored in the ocean with less of an effect on atmospheric CO_2 and fewer adverse effects on the marine environment if the alkalinity of the ocean could be increased, perhaps by dissolving carbonate minerals in seawater. Proposals based on this concept are discussed primarily in Section 6.2.

For ocean storage of CO_2, issues remain regarding environmental consequences, public acceptance, implications of existing laws, safeguards and practices that would need to be developed, and gaps in our understanding of ocean CO_2 storage (Section 6.7, 6.8, and 6.10).

6.1.2 Relevant background in physical and chemical oceanography

The oceans, atmosphere, and plants and soils are the primary components of the global carbon cycle, and actively exchange carbon (Prentice *et al.*, 2001). The oceans cover 71% of the Earth's surface with an average depth of 3,800 m and contain roughly 50 times the quantity of carbon currently contained in the atmosphere and roughly 20 times the quantity of carbon currently contained in plants and soils. The ocean contains so much CO_2 because of its large volume and because CO_2 dissolves in seawater to form various ionic species (Box 6.1).

The increase in atmospheric CO_2 over the past few centuries has been driving CO_2 from the atmosphere into the oceans. The oceans serve as an important sink of CO_2 emitted to the atmosphere taking up on average about 7 $GtCO_2$ yr^{-1} (2 GtC yr^{-1}) over the 20 years from 1980-2000 with ocean uptake over the past 200 years estimated to be > 500 $GtCO_2$ (135 GtC) (Prentice *et al.*, 2001; Sabine *et al.*, 2004). On average, the anthropogenic CO_2 signal is detectable to about 1000 m depth; its near absence in the deep ocean is due to the slow exchange between ocean surface and deep-seawaters.

Ocean uptake of anthropogenic CO_2 has led to a perturbation of the chemical environment primarily in ocean surface waters. Increasing ocean CO_2 concentration leads to decreasing carbonate-ion concentration and increasing hydrogen-ion activity (Box 6.1). The increase in atmospheric CO_2 from about 280 ppm in 1800 to 380 ppm in 2004 has caused an average decrease across the surface of the oceans of about 0.1 *p*H units ($\Delta pH \approx -0.1$) from an initial average surface ocean *p*H of about 8.2. Further increase in atmospheric CO_2 will result in a further change in the chemistry of ocean surface waters that would eventually reach the deep ocean (Figure 6.4). The anthropogenic perturbation of ocean chemistry is greatest in the upper ocean where biological activity is high.

Figure 6.4. Simulated ocean pH changes from CO_2 release to the atmosphere. Modelled atmospheric CO_2 change and horizontally averaged ΔpH driven by a CO_2 emissions scenario: historic atmospheric CO_2 up to 2000, IS92a from 2000 to 2100, and logistic curve extending beyond 2100 with 18,000 $GtCO_2$ (Moomaw et al., 2001) cumulative emissions from 2000 onward (comparable to estimates of fossil fuel resources -- predominantly coal; Caldeira and Wickett, 2003).

Since year 1800, the pH of surface of the oceans has decreased about 0.1 pH units (from an initial average surface ocean pH of about 8.2) and CO_3^{2-} has decreased about 40 μmol/kg. There are a number of pH scales used by ocean chemists and biologists to characterize the hydrogen ion content of seawater, but ΔpH computed on different scales varies little from scale to scale (Brewer et al., 1995).

Most carbon dioxide released to either the atmosphere or the ocean will eventually reside in the ocean, as ocean chemistry equilibrates with the atmosphere (Table 6.1, Figure 6.3). Thus, stabilization of atmospheric CO_2 concentration at levels above the natural level of 280 ppm implies long-term addition of carbon dioxide to the ocean. In equilibrium, the fraction of an increment of CO_2 released that will reside in the ocean depends on the atmospheric CO_2 concentration (Table 6.1; Figure 6.3; Kheshgi *et al.*, 2005; Kheshgi, 2004a).

The capacity of the oceans to absorb CO_2 in equilibrium with the atmosphere is a function of the chemistry of seawater. The rate at which this capacity can be brought into play is a function of the rate of ocean mixing. Over time-scales of decades to centuries, exchange of dissolved inorganic carbon between ocean surface waters and the deep ocean is the primary barrier limiting the rate of ocean uptake of increased atmospheric CO_2. Over many centuries (Kheshgi, 2004a), changes in dissolved inorganic carbon will mix throughout the ocean volume with the oceans containing most of the cumulative CO_2 emissions to the atmosphere/ocean system (Table 6.1; Figure 6.3). Over longer times (millennia), dissolution of $CaCO_3$ causes an even greater fraction of released CO_2 (85-92%) to reside in the ocean (Archer *et al.*, 1997).

Box 6.1. Chemical properties of CO_2.

The oceans absorb large quantities of CO_2 from the atmosphere principally because CO_2 is a weakly acidic gas, and the minerals dissolved in seawater have created a mildly alkaline ocean. The exchange of atmospheric CO_2 with ocean surface waters is determined by the chemical equilibrium between CO_2 and carbonic acid H_2CO_3 in seawater, the partial pressure of CO_2 (pCO_2) in the atmosphere, and the rate of air/sea exchange. Carbonic acid dissociates into bicarbonate ion HCO_3^-, carbonate ion CO_3^{2-}, and hydronium ion H^+ by the reactions (see Appendix A1.3):

$$CO_2\ (gas) + H_2O \leftrightarrow H_2CO_3\ (aqueous) \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+ \qquad (6.1)$$

Total dissolved inorganic carbon (DIC) is the sum of carbon contained in H_2CO_3, HCO_3^-, and CO_3^{2-}. The he atmospheric concentration of CO_2 in equilibrium with surface water can be calculated from well known chemical equilibria that are dominated by equilibria between carbonate species above, and borate species (Zeebe and Wolf-Gladrow, 2001), and, which depend on ocean total dissolved inorganic carbon, alkalinity, temperature and salinity. The partial pressure of CO_2 in the ocean mixed layer equilibrates with the atmosphere on a time scale of about one year.

The ocean is a highly buffered system, i.e. the concentration of the chemical species whose equilibrium controls *p*H is significantly higher than the concentrations of H^+ or OH^-. The *p*H of seawater is the base-10 log of activity of H^+. Total Alkalinity (TAlk) is the excess of alkaline components, and is defined as the amount of strong acid required to bring seawater to the "equivalence point" at which the HCO_3- and H_2CO_3 contributions are equal (Dickson, 1981).

The principal effect of adding CO_2 to seawater is to form bicarbonate ion e.g.

$$CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^- . \qquad (6.2)$$

In addition, some CO_2 undergoes simple reaction with water e.g.,

$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$. (6.3)

In either case, Total Alkalinity does not change. The combined reactions lower both ocean *p*H, and carbonate ion concentration. For current ocean composition, CO_2 that is added to seawater is partitioned primarily into HCO_3^- with the net reaction resulting in the generation of H^+ and thus decreasing *p*H and making seawater more acidic; adding CO_2 thereby decreases the concentration of CO_3^{2-}.

Total Alkalinity is increased when, for example, alkaline minerals such as $CaCO_3$ are dissolved in seawater through the reaction

$CaCO_3$ (solid) $\leftrightarrow Ca^{2+} + CO_3^{2-}$ (6.4)

which releases 2 mole-equivalents of Total Alkalinity and 1 mole of Dissolved Inorganic Carbon for each mole of $CaCO_3$ dissolved. Increasing TAlk more than DIC leads to a decrease in the partial pressure of CO_2 as seen in Figure 6.5. Because most Dissolved Inorganic Carbon is in the form of HCO_3^-, the main effect of dissolving $CaCO_3$ in surface waters is (c.f. Kheshgi, 1995)

$CaCO_3$ (solid) + CO_2 (gas) + $H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$, (6.5)

thereby shifting CO_2 from the atmosphere to the oceans in equilibrium, neutralizing the effect of CO_2 on *p*H.

Figure 6.5. Composition diagram for ocean surface waters at 15 °C (adapted from Baes, 1982). The white lines denote compositions with the same value of pCO_2 (in ppm); the black lines denote compositions with the same pH. The tan shaded region is undersaturated and the green shaded region is supersaturated with respect to calcite at atmospheric pressure (calcite solubility increases with depth). Surface water and average ocean compositions are also indicated. Adding CO_2 increases Dissolved Inorganic Carbon (DIC) without changing Total Alkalinity (TAlk); dissolving $CaCO_3$ increases both DIC and TAlk, with 2 moles of TAlk added for each mole of DIC added.

Ocean surface waters are super-saturated with respect to $CaCO_3$, allowing the growth of corals and other organisms that produce shells or skeletons of carbonate minerals. In contrast, the deepest ocean waters have lower *p*H and lower CO_3^{2-} concentrations, and are thus undersaturated with respect to $CaCO_3$. Marine organisms produce calcium carbonate particles in the surface ocean that settle and dissolve in undersaturated regions of the deep oceans.

Both biological and physical processes lead to the observed distribution of *p*H and its variability in the world ocean (Figure 6.6). As they transit from the Atlantic to Pacific Basins, deep ocean waters accumulate about 10% more dissolved inorganic carbon dioxide, primarily from the oxidation of sinking organic matter (Figure 6.7).

Figure 6.6. Observed variation in open ocean pH for the 1990s (shown on the total hydrogen scale; data from Key et al., 2004). In this figure the oceans are separated into separate panels. The three panels are on the same scale and coloured by latitude band to illustrate the large north-south changes in the pH of intermediate waters. Pre-industrial surface values would have been about 0.1 pH units greater than in the 1990s.

Figure 6.7. Natural variation in dissolved inorganic carbon at 3 km depth. Total dissolved inorganic carbon concentration at 3000 m depth (data from Key et al., 2004). Ocean carbon concentrations increase roughly 10% as deep ocean waters transit from the North Atlantic to the North Pacific due to the oxidation of organic carbon in the deep ocean.

6.2. Approaches to release CO_2 into the ocean

6.2.1 Approaches to releasing CO_2 that has been captured, compressed, and transported into the ocean

6.2.1.1 Basic approach

The basic concept of intentional CO_2 storage in the ocean is to take a stream of CO_2 that has been captured and compressed (Chapter 3), and transport it (Chapter 4) to the deep ocean for release at or above the sea floor. (Other ocean storage approaches are discussed in Sections 6.2.2 and 6.2.3.) Once released, the CO_2 would dissolve into the surrounding seawater, disperse and become part of the ocean carbon cycle.

Marchetti (1977) first proposed injecting liquefied CO_2 into the waters flowing over the Mediterranean sill into the mid-depth North Atlantic, where the CO_2 would be isolated from the atmosphere for centuries. This concept relies on the slow exchange of deep ocean waters with the surface to isolate CO_2 from the atmosphere. The effectiveness of ocean storage will depend on how long CO_2 remains isolated from the atmosphere. Over the centuries and millennia, CO_2 released to the deep ocean will mix throughout the oceans and affect atmospheric CO_2 concentration. The object is to transfer the CO_2 to deep waters because the degree of isolation from the atmosphere generally increases with depth in the ocean. Proposed methods would inject the CO_2 below the thermocline[1] for more effective storage.

Depending on the details of the release and local sea floor topography, the CO_2 stream could be engineered to dissolve in the ocean or sink to form a lake on the sea floor. CO_2, dissolved in seawater at high concentrations, can form a dense plume or sinking current along an inclined sea floor. If release is at a great enough depth, CO_2 liquid will sink and could accumulate on the sea floor as a pool containing a mixture of liquid and hydrate. In the short-term, fixed or towed pipes appear to be the most viable methods for oceanic CO_2 release, relying on technology that is largely already commercially available.

6.2.1.2 Status of development

To date, injection of CO_2 into seawater has been investigated only in the laboratory, in small-scale *in situ* experiments, and in models. Larger-scale *in situ* experiments have not yet been carried out.

An international consortium involving engineers, oceanographers and ecologists from 15 institutions in the United States, Norway, Japan and Canada proposed an *in situ* experiment to help evaluate the feasibility of ocean carbon storage as a means of mitigating atmospheric increases. This was to be a collaborative study of the physical, chemical, and biological changes associated with direct injection of CO_2 into the ocean (Adams *et al.*, 2002). The proposed CO_2 Ocean Sequestration Field Experiment was to inject less than 60 tonnes of pure liquid carbon dioxide (CO_2) into the deep ocean near Keahole Point on the Kona coast of the Island of Hawaii. This would have been the largest intentional CO_2 release into the ocean water column. The test was to have taken place in water about 800 m deep, over a period of about two weeks during the summer of 2001. Total project cost was to have been roughly US$ 5 million. A small steel pipeline, about 4 cm in diameter, was to have been deployed from a ship down to the injection depth with a short section of

[1] The thermocline is the layer of the ocean between about 100 m and 1000 m depth that is stably stratified by large temperature and density gradients, thus inhibiting vertical mixing. Vertical mixing rates in the thermocline can be ~1000 times less that in the deep sea. This zone of slow mixing would act as a barrier to slow degassing of CO_2 to the atmosphere of CO_2 released in the deep ocean.

pipeline resting on the sea floor to facilitate data collection. The liquid CO_2 was to have been dispersed through a nozzle, with CO_2 droplets briefly ascending from the injection point while dissolving into the seawater. However, the project met with opposition from environmental organizations and was never able to acquire all of the necessary permits within the prescribed budget and schedule (de Figueiredo, 2002).

Following this experience, the group developed a plan to release 5.4 tonnes of liquefied CO_2 at a depth of 800 meters off the coast of Norway, and monitor its dispersion in the Norwegian Sea. The Norwegian Pollution Control Authority granted a permit for the experiment. The Conservative Party environment minister in Norway's coalition government, Børge Brende, decided to review the Norwegian Pollution Control Authority 's initial decision. After the public hearing procedure and subsequent decision by the Authority to confirm their initial permit, Brende said, "The possible future use of the sea as storage for CO_2 is controversial. … Such a deposit could be in defiance of international marine laws and the ministry therefore had to reject the application." The Norwegian Environment ministry subsequently announced that the project would not go ahead (Giles, 2002).

Several smaller scale scientific experiments (less than 100 litres of CO_2) have however been executed (Brewer *et al.*, 1999, Brewer *et al.*, 2005) and the necessary permits have been issued also for experiments within a marine sanctuary.

6.2.1.3 Basic behaviour of CO_2 released in different forms

The near-field behaviour of CO_2 released into the ocean depends on the physical properties of CO_2 (Box 6.2) and the method for CO_2 release. Dissolved CO_2 increases the density of seawater (e.g., Bradshaw, 1973; Song, *et al.*, 2005) and this affects transport and mixing. The near field may be defined as that region in which it is important to take into consideration effects of CO_2-induced density changes on the fluid dynamics of the ocean. The size of this region depends on the scale and design of CO_2 release (Section 6.2.1.4).

Box 6.2. Physical properties of CO_2.

The properties of CO_2 in seawater affect its fate upon release to the deep-sea environment. The conditions under which CO_2 can exist in a gas, liquid, solid hydrate, or aqueous phase in seawater are given in Figure 6.8 (see Appendix A1.2).

Figure 6.8. CO_2 phases in seawater. CO_2 is stable in the liquid phase when temperature and pressure (increasing with ocean depth) fall in the region below the blue curve; a gas phase is stable under conditions above the blue dashed line. In contact with seawater and at temperature and pressure in the shaded region, CO_2 reacts with seawater to from a solid ice-like hydrate $CO_2 \bullet 6H_2O$. CO_2 will dissolve in seawater that is not saturated with CO_2. The red line shows how temperature varies with depth at a site off the coast of California; liquid and hydrated CO_2 can exist below about 400 m (Brewer et al., 2004).

At typical pressures and temperatures that exist in the ocean, pure CO_2 would be a gas above approximately 500m and a liquid below that depth. Between about 500 and 2700 m depth, liquid CO_2 is lighter than seawater. Deeper than 3000 m, CO_2 is denser than seawater. The buoyancy of CO_2 released into the ocean determines whether released CO_2 rises or falls in the ocean column (Figure 6.9). In the gas phase, CO_2 is lighter than seawater and rises. In the liquid phase CO_2 is a highly compressible fluid compared to seawater. A fully formed crystalline CO_2 hydrate is denser than seawater and will form a sinking mass (Aya *et al.*, 2003); hydrate formation can thus aid ocean CO_2 storage by more rapid transport to depth, and by slowing dissolution. It may also create a nuisance by impeding flow in pipelines or at injectors.

Figure 6.9. Shallower than 2500 m, liquid CO_2 is less dense than seawater, and thus tends to float upward. Deeper than 3000 m, liquid CO_2 is denser than seawater, and thus tends to sink downward. Between these two depths, the behaviour can vary with location (depending mostly on temperature) and CO_2 can be neutrally buoyant (neither rises nor falls). Conditions shown for the Northwest Atlantic Ocean.

The formation of a solid CO_2 hydrate (Sloan, 1998) is a dynamic process (Figure 6.10; Brewer *et al.*, 1998, 1999, 2000) and the nature of hydrate nucleation in such systems is imperfectly understood. Exposed to an excess of seawater, CO_2 will eventually dissolve forming an aqueous phase with density higher than surrounding seawater. Release of dense, or buoyant, CO_2 — in a gas, liquid, hydrate, or aqueous phase - would entrain surrounding seawater and form plumes that sink, or rise, until dispersed.

Figure 6.10. Liquid CO_2 released at 3600 meters initially forms a liquid CO_2 pool on the sea floor in a small deep-ocean experiment (b, upper picture). In time, released liquid CO_2 reacts with seawater to form (b, lower picture) a solid CO_2 hydrate in a similar pool.

CO_2 plume dynamics depend on the way in which CO_2 is released into the ocean water column. CO_2 can be initially in the form of a gas, liquid, solid or solid hydrate. All of these forms of CO_2 would dissolve into seawater, given enough time (Box 6.1). The dissolution rate of CO_2 in seawater is quite variable and depends on the form (gas, liquid, solid, or hydrate), the depth and temperature of disposal, and the local water velocities. Higher flow rates increase the dissolution rate.

Gas. CO_2 could potentially be released as a gas above roughly 500 m depth (Figure 6.8). Below this depth, pressures are too great for CO_2 to exist as a gas. The gas bubbles would be less dense than the surrounding seawater so tend to rise toward the surface, dissolving at a radial speed of about 0.1 cm hr^{-1} (0.26 to 1.1 μmol cm^{-2} s^{-1}; Teng *et al.*, 1996) In waters colder than about 9°C, a CO_2 hydrate film could form on the bubble wall. CO_2 diffusers could produce gaseous CO_2 bubbles that are small enough to dissolve completely before reaching the surface.

Liquid. Below roughly 500 m depth, CO_2 can exist in the ocean as a liquid. Above roughly 2500 m depth CO_2 is less dense than seawater, so liquid CO_2 released shallower than 2500 m would tend to rise toward the surface. Because most ocean water in this depth range is colder than 9°C, CO_2 hydrate would tend to form on the droplet wall. Under these conditions, the radius of the droplet would diminish at a speed of ~0.5 cm hr^{-1} (= 3 μmol cm^{-2} s^{-1}; Brewer *et al.*, 2002). Under these conditions a 0.9 cm diameter droplet would rise about 400 m in an hour before dissolving completely; 90% of its mass would be lost in the first 200 m (Brewer *et al.*, 2002). Thus, CO_2 diffusers could be designed to produce droplets that will dissolve within roughly 100 m of the depth of release. If the droplet reached approximately 500 m depth, it would become a gas bubble.

CO_2 is more compressible than seawater; below roughly 3000 m, liquid CO_2 is denser than the surrounding seawater and sinks. CO_2 nozzles could be engineered to produce large droplets that would sink to the sea floor or small droplets that would dissolve in the seawater before contacting the sea floor. Natural ocean mixing and droplet motion are expected to prevent concentrations of dissolved CO_2 from approaching saturation, except near liquid CO_2 that has been intentionally placed in topographic depressions on the seafloor.

Solid. Solid CO_2 is denser than seawater and thus would tend to sink. Solid CO_2 surfaces would dissolve in seawater at a speed of about 0.2 cm hr^{-1} (inferred from Aya *et al.*, 1997). Thus small quantities of solid CO_2 would dissolve completely before reaching the sea floor; large masses could potentially reach the sea floor before complete dissolution.

Hydrate. CO_2 hydrate is a form of CO_2 in which a cage of water molecules surrounds each molecule of CO_2. It can form in average ocean waters below about 400 m depth. A fully formed crystalline CO_2 hydrate is denser than seawater and will sink (Aya *et al.*, 2003). The surface of this mass would dissolve at a speed similar to that of solid CO_2, about 0.2 cm hr^{-1} (0.47 to 0.60 μm s^{-1}; Rehder *et al.*, 2004; Teng *et al.*, 1999), and thus droplets could be produced that either dissolve completely in the seawater or sink to the sea floor. Pure CO_2 hydrate is a hard crystalline solid and will not flow through a pipe; however a paste-like composite of hydrate and seawater may be extruded (Tsouris *et al.*, 2004), and this will have a dissolution rate intermediate between those of CO_2 droplets and a pure CO_2-hydrate.

6.2.1.4 Behaviour of injected CO_2 in the near field: CO_2-rich plumes

As it leaves the near field, CO_2 enriched water will reside at a depth determined by its density. The oceans are generally stably stratified with density increasing with depth. Parcels of water tend to move upward or downward until they reach water of the same density; then there are no buoyancy forces to induce further motion.

The dynamics of CO_2-rich plumes determine both the depth at which the CO_2 leaves the near-field environment and the amount of initial dilution (and consequently the amount of *p*H change). When CO_2 is released in any form into seawater, the CO_2 can move upward or downward depending on whether the CO_2 is less or more dense than the surrounding seawater. Drag forces transfer momentum from the CO_2 droplets to the surrounding water column producing motion in the adjacent water, initially in the direction of droplet motion. Simultaneously, the CO_2 dissolves into the surrounding water, making the surrounding water denser and more likely to sink. As the CO_2-enriched water moves, it mixes with surrounding water that is less enriched in CO_2, leading to additional dilution and diminishing the density contrast between the CO_2-enriched water and the surrounding water.

CO_2 releases could be engineered to produce CO_2 plumes with different characteristics (Chen *et al.*, 2003; Sato and Sato, 2002; Alendal and Drange, 2001; Crounse *et al.*, 2001; Drange *et al.,* 2001; Figure 6.11). Modelling studies indicate that releases of small droplets at slow rates produce smaller plumes than release of large droplets at rapid rates. Where CO_2 is denser than seawater, larger droplet sizes would allow the CO_2 to sink more deeply. CO_2 injected at intermediate depths could increase the density of CO_2-enriched seawater sufficiently to generate a sinking plume that would carry the CO_2 into the deep ocean (Liro *et al.*, 1992; Haugan and Drange, 1992). Apparent Coriolis forces would operate on such a plume, turning it towards the right in the Northern Hemisphere and towards the left in the Southern Hemisphere (Alendal *et al.,* 1994). The channelling effects of submarine canyons or other topographic features could help steer dense plumes to greater depth with minimal dilution (Adams *et al.*, 1995).

Figure 6.11. Simulated CO_2 enriched seawater plumes (left panels; indicated by pH) and CO_2 droplet plumes (right panels; indicated by kg CO_2/m^3) created by injecting 1-cm and) 12-cm (top and bottom panels, respectively) liquid CO_2 droplets into the ocean from fixed nozzles (elapsed time is 30 min; d injection rate is 1.0 kg CO_2 /sec; ocean current speed is 5 cm/sec; Alendal and Drange, 2001). By varying droplet size, the plume can be made to sink (top panels) or rise (bottom panels).

The concept of ocean injection from a towed pipe trailing a moving ship was developed in order to minimize the local environmental impacts by accelerating the dissolution and dispersion of injected liquid CO_2 (Ozaki, 1997; Minamiura *et al.*, 2004). A moving-ship could be used to produce a seawater plume with relatively dilute initial CO_2 concentrations (Figures 6.12 and 6.13). In the upper ocean where CO_2 is less dense than seawater, nozzles engineered to produce mm-scale droplets would generate CO_2 plumes that would rise less than 100 m.

Figure 6.12. Simulated plumes (Chen et al., 2005) created by injecting liquid CO_2 into the ocean from a fixed pipe (left panel) and a moving ship (right panel) at a rate of 100 kg/sec (roughly equal to the CO_2 from a 500 MW_e coal-fired power plant). Left panel: injection at 875 m depth (12m from the sea floor) with an ocean current speed of 2.3 cm/sec. Right panel: injection at 1340 m depth from a ship moving at a speed of 3 m/s. Note difference in pH scales; maximum pH perturbations are smaller in the moving ship simulation.

Figure 6.13. Volume of water with a ΔpH less than the value shown on the horizontal axis for the simulations shown in Figure 6.12 corresponding to CO_2 releases from a 500 MW_e power plant. The fixed pipe simulation produces a region with $\Delta pH < -1$; however, the moving ship disperse the CO_2 more widely, largely avoiding pH changes of this magnitude.

6.2.1.5 Behaviour of injected CO_2 in the far field

The far field is defined as the region in which the concentration of added CO_2 is low enough such that the resulting density increase does not significantly affect transport, and thus CO_2 may be considered a passive tracer in the ocean. Typically, this would apply within a few kilometres of an injection point in midwater, but if CO_2 is released at the seafloor and guided along topography, concentration may remain high and influence transport for several tens of kilometres. CO_2 is transported by ocean currents and undergoes further mixing and dilution with other water masses (Masuda *et al.*, 2004). Most of this mixing and transport occurs along surfaces of nearly constant density, because buoyancy forces inhibit vertical mixing in a stratified fluid. Over time, a release of CO_2 becomes increasingly diluted but affects ever greater volumes of water.

Ocean general circulation models have been used to predict changes in ocean chemistry resulting from the dispersion of injected CO_2 for hypothetical examples of ocean storage (e.g., Orr, 2004). Wickett *et al.* (2003) estimated that injection into the deep ocean at a rate of 0.37 $GtCO_2\ yr^{-1}$ (= 0.1 $GtC\ yr^{-1}$) for 100 years would produce a $\Delta pH < -0.3$ over a volume of seawater equivalent to 0.01 % or less of total ocean volume (Figure 6.14). In this example, for each $GtCO_2$ released to the deep ocean, less than ~0.0001 %, 0.001%, and 0.01 % of the ocean volume has Δ*p*H of less than -0.3, -0.2, and -0.1 *p*H units, respectively. Caldeira and Wickett (2005) predicted volumes of water undergoing a range of *p*H changes for several atmospheric emission and carbon stabilization pathways, including pathways in which direct injection of CO_2 into the deep ocean was assumed to provide either 10% or 100% of the total atmospheric CO_2 mitigation effort needed to stabilize atmospheric CO_2 according to the WRE550 pathway assuming a CO_2 production scenario in which all known fossil-fuel resources are ultimately combusted. Simulations in which ocean injection provided 10% of the total mitigation effort resulted in significant changes in ocean *p*H in year 2100 over roughly 1% of the ocean volume (Figure 6.15); by year 2300, injection rates have slowed but previously injected carbon has spread through much of the ocean resulting in an additional 0.1 *p*H unit reduction in ocean *p*H over most of the ocean volume compared to WRE550.

Figure 6.14. Estimated volume of pH perturbations at basin scale (Wickett et al., 2003. Simulated fraction of global ocean volume with a ΔpH less than the amount shown on the horizontal axis, after

100 years of simulated injection at a rate of 0.37 $GtCO_2$ yr^{-1} (= 0.1 GtC yr^{-1}) at each of four different points (two different depths near New York City and San Francisco). Model results indicate, for example, that injecting CO_2 at this rate at a single location for 100 years could be expected to produce a volume of seawater with a $\Delta pH < -0.3$ units in 0.01% or less of total ocean volume (0.01 % of the ocean is roughly 10^5 km^3). As with other simulations of direct CO_2 injection in the ocean, results for the upper ocean (e.g., 800 m) tend to be more site-specific than are results for the deep ocean (e.g., 3000 m).

Figure 6.15. Estimated volume of pH perturbations at global scale for hypothetical examples in which injection of CO_2 into the ocean interior provides 100% or 10% of the mitigation effort needed to move from a logistic emissions curve cumulatively releasing 18,000 $GtCO_2$ (=5000 GtC) to emissions consistent with atmospheric CO_2 stabilization at 550 ppm according to the WRE550 pathway (Wigley et al., 1996). Simulated fraction of ocean volume with a pH reduction greater than the amount shown on the horizontal axis. For the 10% case, in year 2100, injection rates are high and on the order of 1% of the ocean volume has significant pH reductions; in year 2300, injection rates are low, but previously injected CO_2 has decreased ocean pH by about 0.1 unit below the value produced by a WRE550 atmospheric CO_2 pathway in the absence of CO_2 release directly to the ocean. (Caldeira and Wickett, 2005).

6.2.1.6 Behaviour of CO_2 lakes on the sea floor

Long-term storage of carbon dioxide might be more effective if CO_2 were stored on the sea floor in liquid or hydrate form below 3000 meters, where CO_2 is denser than seawater (Box 6.2; Ohsumi, 1995; Shindo *et al.*, 1995). Liquid carbon dioxide could be introduced at depth to form a lake of CO_2 on the sea floor (Ohsumi, 1993). Alternatively, CO_2 hydrate could be created in an apparatus designed to produce a hydrate pile or pool on the sea floor (Saji *et al.*, 1992). To date, the concept of CO_2 lake on the sea floor has been investigated only in the laboratory, in small-scale (tens of litres) *in situ* experiments, and in numerical models. Larger-scale *in situ* experiments have not yet been carried out.

Liquid or hydrate deposition of CO_2 on the sea floor could increase isolation, however, in the absence of a physical barrier, the CO_2 would dissolve into the overlying water (Mori and Mochizuki, 1998; Haugan *et al.*, 2005). In this aspect, most sea floor deposition proposals can be viewed as a means of "time-delayed release" of CO_2 into the ocean; thus, many issues relevant to sea floor options, especially the far-field behaviour, are discussed in sections relating to CO_2 release into the water column (e.g., Section 6.2.1.5).

CO_2 released onto the sea floor deeper than 3 km is denser than surrounding seawater is expected to fill topographic depressions, accumulating as a lake of CO_2 over which a thin hydrate layer would form. This hydrate layer would retard dissolution, but it would not insulate the lake from the overlying water. The hydrate would dissolve into the overlying water (or sink to the bottom of the CO_2 lake), but the hydrate layer would be continuously renewed through the formation of new crystals (Mori, 1998). Laboratory experiments (Aya *et al.*, 1995) and small deep-ocean experiments (Brewer *et al.*, 1999) show that deep-sea storage of CO_2 would lead to CO_2 hydrate formation (and subsequent dissolution).

Predictions of the fate of large-scale CO_2 lakes rely on numerical simulations because no large-scale field experiments have yet been performed. For a CO_2 lake with an initial depth of 50 m, the time of complete dissolution varies from 30 to 400 years depending on the local ocean and sea floor environment. The time to dissolve a CO_2 lake depends on its depth, complex dynamics of the ocean bottom boundary layer and its turbulence characteristics, mechanism of CO_2 hydrate dissolution,

and properties of CO_2 in solution (Haugan and Alendal, 2005). The lifetime of a CO_2 lake would be longest in relatively confined environments, such as might be found in some trenches or depressions with restricted flow (Ohgaki and Akano, 1992). (Strong flows have been observed in trenches (Nakashiki, 1997). Nevertheless, simulation of CO_2 storage in a deep trench (Kobayashi, 2003) indicate that the bottom topography can weaken vertical momentum and mass transfer, slowing the CO_2 dissolution rate. In a quiescent environment, transport would be dominated by diffusion; double-diffusion in the presence of strong stratification may produce long lake lifetimes. In contrast, the flow of seawater across the lake surface would increase mass transfer and dissolution. For example, CO_2 lake lifetimes of >10,000 yr for a 50 m-thick lake can be estimated from the dissolution rate of 0.44 cm yr^{-1} for a quiescent, purely diffusive system (Ohsumi, 1997). Fer and Haugan (2003) found that a mean horizontal velocity of 0.05m/sec would cause the CO_2 lake to dissolve >25 times more rapidly (12 cm yr^{-1}). Furthermore, they found that an ocean bottom storm with a horizontal velocity of 0.20 m/sec could increase the dissolution rate to 170 cm yr^{-1}.

6.2.2 CO_2 storage by dissolution of carbonate minerals

Over thousands of years, increased seawater acidity resulting from CO_2 addition will be largely neutralized by the slow natural dissolution of carbonate minerals in sea-floor sediments and on land. This neutralization allows the ocean to absorb more CO_2 from the atmosphere with less of a change in ocean *p*H, carbonate ion concentration, and pCO_2 (Archer *et al.*, 1997, 1998). Various approaches have been proposed to accelerate carbonate neutralization, and thereby store CO_2 in the oceans, by promoting the dissolution of carbonate minerals[2]. These approaches (e.g., Kheshgi, 1995; Rau and Caldeira, 1999) do not entail initial, separate, CO_2 capture and transport steps. However, no tests of these approaches have yet been performed at sea, so inferences about enhanced ocean CO_2 storage, and effects on ocean *p*H are based on laboratory experiments (Morse and Mackenzie, 1990; Morse and Arvidson, 2002), calculations (Kheshgi, 1995), and models (Caldeira and Rau, 2000).

Carbonate neutralization approaches attempt to promote Reaction 6.5 (see Box 6.1) in which limestone reacts with carbon dioxide and water to form calcium and bicarbonate ions in solution. Accounting for speciation of dissolved inorganic carbon in seawater (Kheshgi, 1995), for each mole of $CaCO_3$ dissolved there would be 0.8 mole of additional CO_2 stored in seawater in equilibrium with fixed CO_2 partial pressure (i.e., ~2.8 tonnes of limestone per tonne CO_2). Adding alkalinity to the ocean would increase ocean carbon storage, both in the near term and on millennial time scales (Kheshgi, 1995). The duration of increased ocean carbon storage would be limited by eventual $CaCO_3$ sedimentation, or reduced $CaCO_3$ sediment dissolution, which is modelled to occur through natural processes on the time scale of about 6,000 years (Archer *et al.*, 1997, 1998).

Carbonate minerals have been proposed as the primary source of alkalinity for neutralization of CO_2 acidity (Kheshgi 1995; Rau and Caldeira, 1999). There have been many experiments and observations related to the kinetics of carbonate mineral dissolution and precipitation, both in fresh water and in seawater (Morse and Mackenzie, 1990; Morse and Arvidson, 2002). Carbonate minerals and other alkaline compounds that dissolve readily in surface seawater (such as Na_2CO_3), however, have not been found in sufficient quantities to store carbon in the ocean on scales comparable to fossil CO_2 emissions (Kheshgi, 1995). Carbonate minerals that are abundant do not dissolve in surface ocean waters. Surface ocean waters are typically oversaturated with respect to

[2] This approach is fundamentally different than the carbonate mineralization approach assessed in Chapter 7. In that approach CO_2 is stored by reacting it with non-carbonate minerals to form carbonate minerals. In this approach, carbonate minerals are dissolved in the ocean, thereby increasing ocean alkalinity and increasing ocean storage of CO_2. This approach could also make use of non-carbonate minerals, if their dissolution would increase ocean alkalinity.

carbonate minerals (Broecker and Peng, 1982; Emerson and Archer, 1990; Archer, 1996), but carbonate minerals typically do not precipitate in seawater due to kinetic inhibitions (Morse and Mackenzie, 1990).

To circumvent the problem of oversaturated surface waters, Kheshgi (1995) considered promoting reaction (6.5) by calcining limestone to form CaO, which is readily soluble. If the energy for the calcining step was provided by a CO_2-emission-free source, and the CO_2 released from $CaCO_3$ were captured and stored (e.g. in a geologic formation), then this process would store 1.8 mole CO_2 per mole CaO introduced into the ocean. If the CO_2 from the calcining step were not stored, then a net 0.8 mole CO_2 would be stored per mole CaO. However, if coal without CO_2 capture were used to provide the energy for calcination, and the CO_2 produced in calcining was not captured, only 0.4 mole CO_2 would be stored net per mole lime (CaO) to the ocean, assuming existing high-efficiency kilns (Kheshgi, 1995). This approach would increase the ocean sink of CO_2, and does not need to be connected to a concentrated CO_2 source or require transport to the deep sea. Such a process would, however, need to avoid rapid re-precipitation of $CaCO_3$, a critical issue yet to be addressed.

Rau and Caldeira (1999) proposed extraction of CO_2 from flue gas via reaction with crushed limestone and seawater. Exhaust gases from coal-fired power plants typically have 0.15 atm partial pressure of CO_2 over 400 times that of ambient air. A carbonic acid solution formed by contacting seawater with flue gases would accelerate the dissolution of calcite, aragonite, dolomite, limestone, and other carbonate-containing minerals, especially if minerals were crushed to increase reactive surface area. The solution of, for example, Ca^{2+} and dissolved inorganic carbon (primarily in the form of HCO_3^-) in seawater could then be released back into the ocean, where it would be diluted by additional seawater. Caldeira and Rau (2000) estimate that dilution of one part effluent of a carbonate neutralization reactor with 100 parts ambient seawater would result, after equilibration with the atmosphere, in a 10% increase in the calcite saturation state, which they contend would not induce precipitation. This approach does not rely on deep-sea release, avoiding the need for energy to separate, transport and inject CO_2 into the deep ocean. The wastewater generated by this carbonate-neutralization approach has been conjectured to be relatively benign (Rau and Caldeira, 1999). For example, the addition of calcium bicarbonate, the primary constituent of the effluent, has been observed to promote coral growth (Marubini and Thake, 1999). This approach will not remove all the CO_2 from a gas stream, because excess CO_2 is required to produce a solution that is corrosive to carbonate minerals. If greater CO_2 removal were required, this approach could be combined with other techniques of CO_2 capture and storage.

Process wastewater could be engineered to contain different ratios of added carbon and calcium, and different ratios of flue gas CO_2 to dissolved limestone (Caldeira and Wickett, 2005). Processes involving greater amounts of limestone dissolution per mole CO_2 added lead to a greater CO_2 fraction retained. The effluent from a carbonate-dissolution reactor could have the same *p*H, pCO_2, or $[CO_3^{2-}]$ as ambient seawater, although processing costs may be reduced by allowing effluent composition to vary from these values (Caldeira and Rau, 2000). Elevation in Ca^{2+} and bicarbonate content from this approach is anticipated to be small relative to the already existing concentrations in seawater (Caldeira and Rau, 2000), but effects of the new physicochemical equilibria on physiological performance are unknown. Neutralization of carbon acidity by dissolution of carbonate minerals could reduce impacts on marine ecosystems associated with *p*H and CO_3^{2-} decline (Section 6.7).

Carbonate neutralization approaches require large amounts of carbonate minerals. Sedimentary carbonates are abundant with estimates of 5×10^{17} tonnes (Berner *et al.*, 1989), roughly 10,000 times greater than the mass of fossil fuel carbon. Nevertheless, up to about 1.5 mole of carbonate

mineral must be dissolved for each mole of anthropogenic CO_2 permanently stored in the ocean (Caldeira and Rau, 2000); therefore, the mass of $CaCO_3$ used would be up to 3.5 times the mass of CO_2 stored. Worldwide, 3 Gt $CaCO_3$ is mined annually (Kheshgi, 1995). Thus, large-scale deployment of carbonate neutralization approaches would require greatly expanded mining and transport of limestone and attendant environmental impacts. In addition, impurities in dissolved carbonate minerals may cause deleterious effects and have yet to be studied.

6.2.3 Other ocean storage approaches

Solid hydrate. Water reacts with concentrated CO_2 to form a solid hydrate (CO_2.6H2O) under typical ocean conditions at quite modest depths (Løken and Austvik, 1993; Holdren and Baldwin, 2001). Rehder *et al.* (2004) showed that the hydrate dissolves rapidly into the relatively dilute ocean waters. The density of pure CO_2 hydrate is greater than seawater, and this has led to efforts to create a sinking plume of released CO_2 in the ocean water column. Pure CO_2 hydrate is a hard crystalline solid and thus will not flow through a pipe, and so some form of a CO_2 slurry is required for flow assurance (Tsouris *et al.*, 2004).

Water-$CaCO_3$-CO_2 emulsion. Mineral carbonate could be used to physically emulsify and entrain CO_2 injected in seawater (Swett *et al.* 2004); a 1:1 CO_2:$CaCO_3$ emulsion of CO_2 in water could be stabilized by pulverized limestone ($CaCO_3$). The emulsion plume would have a bulk density of 40% greater than that of seawater. Because the emulsion plume is heavier than seawater, the $CaCO_3$-coated CO_2 slurries may sink all the way to the ocean floor. It has been suggested that the emulsion plume would have a *p*H that is at least 2 units higher than would a plume of liquid CO_2. Carbonate minerals could be mined on land, and then crushed, or fine-grained lime mud could be extracted from the sea floor. These fine-grain carbonate particles could be suspended in seawater upstream from the CO_2-rich plume emanating from direct CO_2 injection site. The suspended carbonate minerals could then be advected with the ambient seawater into the plume, where the minerals could dissolve, increasing the effectiveness ocean CO_2 storage and diminishing the *p*H impacts of direct injection.

Emplacement in carbonate sediments. Murray *et al.* (1997) have suggested emplacement of CO_2 into carbonate sediments on the sea floor. Insofar as this CO_2 remained isolated from the ocean, this could be categorized as a form of geologic storage (Chapter 5).

Dry ice torpedoes. CO_2 could be released from a ship as dry ice at the ocean surface (Steinberg,1985). One costly method is to produce solid CO_2 blocks (Murray *et al.*, 1996). With a density of 1.5 t/m^3, these blocks would sink rapidly to the sea floor and could potentially penetrate into the sea floor sediment.

Direct flue gas injection. Another proposal is to take a power plant flue gas, and pump it directly into the deep ocean without any separation of CO_2 from the flue gas; however, costs of compression are likely to render this approach infeasible.

6.3. Capacity and fractions retained

6.3.1 Capacity

The physical capacity for storage of CO_2 in the ocean is large relative to fossil fuel resources; the degree to which this capacity will be utilized may be based on factors such as cost, equilibrium pCO_2, and environmental consequences.

Storage capacity for CO_2 in the ocean can be defined relative to an atmospheric CO_2 stabilization concentration. For example, roughly 2,300 to 10,700 $GtCO_2$ would be added to the ocean (above the natural pre-industrial background) in equilibrium with atmospheric CO_2 stabilization concentrations ranging from 350 ppm to 1000 ppm, regardless of whether the CO_2 is initially released to the ocean or the atmosphere. (Table 6.1, Figure 6.3; Kheshgi *et al.*, 2005; Sorai and Ohsumi, 2005). The capacity of the ocean for CO_2 storage could be increased with the addition of alkalinity to the ocean (e.g., dissolved limestone).

6.3.2 Measures of fraction retained

Effectiveness of ocean CO_2 storage has been reported in a variety of ways. These different ways of reporting result in very different numerical values (Box 6.3).

Box 6.3. Measures of the fraction retained in storage of CO_2

Different measures have been used to describe how effective intentional storage of carbon dioxide in the ocean is to mitigate climate change (Mueller *et al.*, 2004). Here, we illustrate several of these measures using schematic model results reported by Herzog *et al.* (2003) for injection of CO_2 at three different depths (Figure 6.16).

Figure 6.16. Fraction of carbon in the ocean from injection at three different depths and the atmosphere illustrated with results from a schematic model (Herzog et al., 2003). Calculations assume a background 280 ppm of CO_2 in the atmosphere. Solid lines = retained fraction; Dashed lines = airborne fraction. Grey dashed line = airborne fraction for release to atmosphere.

Fraction retained (see chapter 1) is the fraction of the cumulative amount of injected CO_2 that is retained in the storage reservoir over a specified period of time, and thereby does not have the opportunity to affect atmospheric CO_2 concentration (Mignone *et al.*, 2004). Retained fraction approaches zero (Figure 6.16) over long times indicating that nearly all injected CO_2 will interact with the atmosphere (although a small amount would interact first with carbonate sediments).

Airborne Fraction is the fraction of released CO_2 that adds to atmospheric CO_2 content (Kheshgi and Archer, 2004). For atmospheric release, airborne fraction is initially one and decays to roughly 0.2 (depending on atmospheric CO_2 concentration) as the added CO_2 is mixed throughout the ocean, and decays further to about 0.08 as CO_2 reacts with sediments (Archer *et al.*, 1997). For deep-sea release, airborne fraction is initially zero and then approaches that of atmospheric release. Note that the asymptotic airborne fraction depends on the concentration of CO_2 of surface waters (Figure 6.3).

Fraction retained is used throughout this report to indicate how long the CO_2 is stored. The following measures, in addition, can be used to compare the effectiveness of ocean carbon storage with other options, e.g.:

- The **Net Present Value** (NPV) approach (Herzog *et al.*, 2003) considers temporary storage to be equivalent to delayed emission of CO_2 to the atmosphere. The value of delaying CO_2 emissions depends on the future costs of CO_2 emission and economic discount rates. There is economic value to temporary storage (i.e., delayed emission) if the cost of CO_2 emissions increases at a rate that is less than the discount rate (Herzog *et al.*, 2003).
- The **Global Warming Potential** (GW_p) is a measure defined by the IPCC to compare the climatic effect of different greenhouse gas emissions. It is computed by integrating the radiative climate forcing of a greenhouse gas emission out to a specified time horizon. This measure has been applied to compare the radiative forcing from oceanic and atmospheric releases of carbon dioxide (Kheshgi *et al.*, 1994, Ramaswamy *et al.*, 2001). Haugan and Joos (2004) propose a modification to the GWP approach that compares the climate effects of the airborne fraction of a CO_2 release to the ocean with those from a release to the atmosphere.

Table 6.2 compares these measures for results from a schematic model at three depths.

Table 6.2. Evaluation of measures described in the text illustrated using schematic model results shown in Figure 6.16. For the Net Present Value measure, the percentage represents the discount rate minus the rate of increase in the cost of CO_2 emission. (If these are equal, the Net Present Value of temporary carbon storage is zero.) Two significant digits shown for illustration exceed the accuracy of model results.

Over several centuries, CO_2 released to the deep ocean would be transported to the ocean surface and interact with the atmosphere; the CO_2-enriched water would then exchange CO_2 with the atmosphere as it approaches chemical equilibrium. In this chemical equilibrium, most of the injected CO_2 remains in the ocean even though it is no longer isolated from the atmosphere (Table 6.1; Figure 6.3). CO_2 that has interacted with the atmosphere is considered to be part of the natural carbon cycle, much in the way that CO_2 released directly to the atmosphere is considered to be part of the natural carbon cycle. Such CO_2 cannot be considered to be isolated from the atmosphere in a way that can be attributable to an ocean storage project.

Loss of isolation of injected CO_2 does not mean loss of all of the injected CO_2 to the atmosphere. In chemical equilibrium with an atmosphere containing 280 ppm CO_2, ~85% of any carbon injected would remain the ocean. If atmospheric CO_2 partial pressures were to approach 1000 ppm, ~66% of the CO_2 injected CO_2 would remain in the ocean after equilibration with the atmosphere (Table 6.1). Thus, roughly 1/5 to 1/3 of the CO_2 injected into the ocean will eventually reside in the atmosphere, with this airborne fraction depending on the long-term atmosphere-ocean CO_2 equilibrium (Kheshgi, 1995, 2004b). The airborne fraction is the appropriate measure to quantify the effect of ocean storage on atmospheric composition.

6.3.3 Estimation of fraction retained from ocean observations

Observations of radiocarbon, CFCs, and other tracers indicate the degree of isolation of the deep sea from the atmosphere (Prentice *et al.*, 2001). Radiocarbon is absorbed by the oceans from the atmosphere and is transported to the deep-sea, undergoing radioactive decay as it ages. Radiocarbon age (Figure 6.17) is not a perfect indicator of time since a water parcel last contact the atmosphere because of incomplete equilibration with the atmosphere (Orr, 2004). Taking this partial equilibration into account, the age of North Pacific deep water is estimated to be in the range of 700 to 1000 years. Other basins, such as the North Atlantic, have characteristic over-turning times of 300 years or more. These data suggest that, generally, carbon injected in the deep ocean would equilibrate with the atmosphere on a time-scale of 300 to 1000 years.

Figure 6.17. Map of radiocarbon (^{14}C) age at 3500 m (Matsumoto and Key, 2004).

6.3.4 Estimation of fraction retained from model results

Ocean models have been used to predict the isolation of injected CO_2 from the atmosphere. Many models are calibrated using ocean radiocarbon data, so model based estimates of retention of injected CO_2 are not completely independent of the estimates based more directly on observations (Section 6.3.3).

A wide number of studies have used three-dimensional ocean general circulation models to study retention of CO_2 injected into the ocean water column (Bacastow and Stegen, 1991; Bacastow *et al.*, 1997; Nakashiki and Ohsumi, 1997; Dewey *et al.*, 1997, 1999; Archer *et al.*, 1998; Xu *et al.*, 1999;

Orr, 2004; Hill *et al.*, 2004). These modelling studies generally confirm inferences based on simpler models and considerations of ocean chemistry and radiocarbon decay rates. In ocean general circulation simulations performed by seven modelling groups (Orr, 2004), CO_2 was injected for 100 years at each of seven different locations and at three different depths. Model results indicate that deeper injections will be isolated from the atmosphere for longer durations. Figure 6.17 shows the effect of injection depth on retained fraction for the mean of seven ocean sites (Orr, 2004). Ranges of model results indicate some uncertainty in forecasts of isolation of CO_2 released to the deep ocean, although for all models the time extent of CO_2 isolation is longer for deeper CO_2 release, and isolation is nearly complete for 100 years following CO_2 release at 3000 m depth (Figure 6.18 and 6.19). However, present-day models disagree as to the degassing time scale for particular locations (Figure 6.19). There seems to be no simple and robust correlate of CO_2 retention other than depth of injection (Caldeira *et al.*, 2002), however, there is some indication that the mean fraction retained for stored carbon is greater in the Pacific Ocean than the Atlantic Ocean, but not all models agree on this. Model results indicate that for injection at 1500 m depth, the time scale of the partial CO_2 degassing are sensitive to the location of the injection, but, at 3000 m, results are relatively insensitive to injection location. Model results have been found to be sensitive to differences in numerical schemes and model parameterizations (Mignone *et al.*, 2004).

Figure 6.18. Results are shown for seven ocean general circulation models at three different depths averaged over seven injection locations (Orr, 2004). The % efficiency shown is the retained fraction for an injection at a constant rate from 2000 to 2100. Models agree that deeper injection isolates CO_2 from the atmosphere longer than shallower injection. For release at 3000 m, most of the added carbon was still isolated from the atmosphere at the end of the 500 year simulations.

Figure 6.19. Comparison of storage results for three injection locations (at 3000 m depth) in ten ocean model simulations (Orr, 2004). Models differ on predictions of CO_2 fraction retained for release at in different oceans.

These ocean general circulation model calculations did not consider interactions with $CaCO_3$ sediments or marine biota. Increased CO_2 concentrations in the ocean promote dissolution of $CaCO_3$ sediments, which would tend to increase predicted CO_2 retention. This has been modelled for the deep-sea with results of greater retention for release in the Atlantic because of high $CaCO_3$ inventory in Atlantic sediments (Archer *et al.*, 1998).

Preliminary numerical simulations of ocean CO_2 injection predict show increased oceanic retention of injected CO_2 with concurrent global warming due to weaker overturning and a more stratified ocean (Jain and Cao, 2005). Some evidence indicates recent increases in stratification in all major ocean basins (e.g. Joos, 2003; McPhaden and Zhang, 2002; Palmer *et al.*, 2004; Stramma *et al.*, 2004).

6.4. Site selection

6.4.1 Background

There are no published papers specifically on site selection for intentional ocean storage of CO_2; hence, we can discuss only general factors that might be considered when selecting sites for ocean storage. Among these considerations are environmental consequences, costs, safety, and international issues (including cross border transport). Because environmental consequences, costs, and social and political issues are addressed in other parts of this report, here we briefly consider site selection factors that enhance the fraction retained or reduce the costs.

6.4.2 Water column release

Large point sources of CO_2 located near deep water would generally be the most cost effective settings in which to carry out direct CO_2 injection (Figure 6.21; Section 6.9). While models indicate that site-specific differences exist, they do not yet agree on the ranking of potential sites for effectiveness of direct injection CO_2 operations (Orr, 2004).

Figure 6.20. For the ocean, location of water at least 1 km and 3 km deep; for land, distance to water that is at least 3 km deep (Caldeira and Wickett, 2005). In general, land areas with the lightest colours would be the most-cost effective land-based settings for a CO_2-injection operation. However, each potential site would need to be evaluated prior to deployment.

6.4.3 CO_2 lakes on the sea floor

CO_2 lakes must be on the sea floor at a depth below 3000 m (Figures 6.20 and 6.21), because the liquid CO_2 must be denser than surrounding seawater (Box 6.2).

Figure 6.21. Relationship between depth and sea floor area.

Flow in ocean bottom boundary layers would need to be taken into account when selecting a site for a CO_2 lake. Bottom friction and turbulence can enhance the dissolution rate and vertical transportation of dissolved CO_2 and lead to a short lifetime for the lake (Section 6.2.1.6). It has been suggested that CO_2 lakes would be preferentially sited in relatively restricted depressions or a trenches on sea floor (Ohsumi, 1995).

6.4.4 Limestone neutralization

The amounts of seawater and limestone required to neutralize the acidity of added CO_2 indicate that limestone neutralization would be most suitable for CO_2 point sources located near both the ocean and large deposits of limestone (Rau and Caldeira, 1999).

6.5. Injection technology and operations

6.5.1 Background

The development of ocean storage technology is generally at a conceptual stage; thus, we discuss only general principles. There has been limited engineering analysis and experimental studies of these conceptual technologies for ocean storage (Nihous, 1997), and no field-testing. No operational experience exists. Various technology concepts have been proposed to improve isolation from the atmosphere or diminish environmental consequences of CO_2 injected into the ocean. Further research and development would be needed to make technologies available, but no major technical barriers are apparent.

6.5.2 Water column release

Dispersal of liquid CO_2 at a depth of 1000m or deeper is technologically feasible. Since liquid CO_2 may be relatively easily transported to appropriate depths, the preferred release mode is thought at this time to be as a liquid or dense gas phase (achieved by compression beyond its critical point, 72.8 bar at 31°C). The pipes that would carry this CO_2 to the deep ocean would be similar to the pipes that have been used commercially on land to transport CO_2 for use in CO_2 enhanced oil recovery projects (Ozaki *et al.*, 1997). Models (Liro *et al.*, 1992, Drange and Haugan, 1992) predict that, with a properly designed diffuser, nearly all the CO_2 would dissolve in the ocean within a

100m of the injection depth. Then, this CO_2-rich water would be diluted as it disperses, primarily horizontally along surfaces of constant density.

Water column injection schemes typically envision minimizing local changes to ocean chemistry by producing a relatively dilute initial injection through a series of diffusers or by other means. Dilution would reduce exposure of organisms to very low *p*H (very high CO_2) environments (Section 6.7).

One set of options for releasing CO_2 to the ocean involves transporting liquid CO_2 from shore to the deep ocean in a pipeline. This would not present any major new problems in design, "according to petroleum engineers and naval architects speaking at one of the IEA Greenhouse Gas R&D Programme ocean storage workshops" (Ormerod *et al.*, 2002). The oil industry has been making great advances in undersea offshore technology, with projects routinely working at depths greater than 1000 m. The oil and the gas industry already places pipes on the bottom of the sea in depths down to 1600 m, and design studies have shown 3000 m to be technically feasible (Ormerod *et al.*, 2002). The 1-m diameter pipe would have the capacity to transport 70,000 tCO_2/day, enough for CO_2 captured from 3GWe of a coal-fired electric power (Ormerod *et al.*, 2002). Liro *et al.* (1992) proposed injecting liquid CO_2 at a depth of about 1000m from a manifold lying near the ocean bottom to form a rising droplet plume. Nihous *et al.* (2002) proposed to inject liquid CO_2 at a depth of below 3000m from a manifold lying near the ocean bottom and form a sinking droplet plume. Engineering work would need to be done to assure that, below 500 m depth, hydrates do not form inside the discharged pipe and nozzles, as this could block pipe or nozzle flow.

CO_2 could be transported by tanker for release from a stationary platform (Ozaki *et al.*, 1995) or through a towed pipe (Ozaki *et al.*, 2001). In either case, the design of CO_2-tankers would be nearly identical to those, which are now used to transport liquid petroleum gas (LPG). Cooling would be used, in order to reduce pressure requirements, with design conditions of -55 degrees C and 6 bar pressure (Ormerod *et al.*, 2002). Producing a dispersed initial concentration would diminish the magnitude of the maximum *p*H excursion. This would probably involve designing for size of the initial liquid CO_2 droplet and the turbulent mixing behind the towed pipe (Tsushima *et al.*, 2002). Diffusers could be designed so that CO_2 droplets would dissolve completely before it reaches the liquid-gas phase boundary.

CO_2 hydrate is about 15% denser than seawater, so it would tend to sink, dissolving into seawater over a broad depth horizon (Wannamaker and Adams, 2002). Kajishima *et al.* (1997) and Saito *et al.* (2001) investigated a proposal to create a dense CO_2-seawater mixture at a depth of between 500 and 1000 m to form a sinking bottom gravity current. Another proposal (Tsouris *et al.*, 2004; West *et al.*, 2003) envisions releasing a sinking CO_2-hydrate/seawater slurry at between 1000 and 1500 m depth. This sinking plume would dissolve as it sinks, potentially distributing the CO_2 over kilometres of vertical distance, and achieving some fraction of the CO_2 retained in deep storage despite the initial release into intermediate waters. The production of a hydrate/seawater slurry has been experimentally demonstrated at sea (Tsouris *et al.*, 2004). Tsouris *et al.* (2004) have carried out a field experiment at 1000m ocean depth in which rapid mixing of seawater with CO_2 in a capillary nozzle a neutrally buoyant composite paste, thus enhancing ocean retention time over that from creation of a buoyant plume. Aya *et al.* (2004) have shown that a rapidly sinking plume of CO_2 can be formed by release of a slurry combining cold liquid, and solid, CO_2 with a hydrate skin. This would effectively transfer ship released CO_2 at shallow ocean depth to the deep ocean without the cost of a long pipe. In all of these schemes the fate of the CO_2 is to be dissolved into the ocean, with increased depth of dissolution, and thus increased retention.

6.5.3 Production of a CO_2 lake

Nakashiki *et al.* (1997) investigated several different kinds of discharge pipes that could be used from a liquid CO_2 tanker to create a CO_2 lake on the sea floor. They concluded that a "floating discharge pipe" might be the best option because it is simpler than the alternatives and less likely to be damaged by wind and waves in storm conditions.

Aya *et al.* (2003) proposed creating a slurry of liquid CO_2 mixed with dry ice and releasing into the ocean at around 200 to 500 m depth. The dry ice is denser that the surrounding seawater and would cause the slurry to sink. An *in situ* experiment carried out off the coast of California found that a CO_2 slurry and dry ice mass with initial diameter about 8.0 cm sank approximately 50 meters within two minutes before the dry ice melted (Aya *et al.*, 2003). The initial size of CO_2 slurry and dry ice is a critical factor making it possible to sink more than 3000 m to the sea floor. To meet performance criteria, the dry ice content would be controlled with a system consisting of a main power engine, a compressor, a condenser, and some pipe systems.

6.6. Monitoring and verification

6.6.1 Background

Monitoring (Figure 6.22) would be done for at least two different purposes: (1) to gain specific information relating to a particular CO_2 storage operation and (2) to gain general scientific understanding. A monitoring program should attempt to quantify the mass and distribution of CO_2 from each point source, and could record related biological and geochemical parameters. These same issues may relate to monitoring of potential leakages from sub-sea geologic storage, or for verification that such leakage does not occur. Monitoring protocols for e.g. submarine sewage disposal are already well established, and experience may be drawn from that.

Figure 6.22. Schematic of possible approaches for monitoring the injection of CO_2 into the deep ocean via a pipeline. The grey region represents a plume of high CO_2/low pH water extending from the end of the pipeline. Shown at the end of the pipeline are two sets of chemical, biological, and current sensors and two underwater cameras. An array of moored sensors can be seen around the pipe to monitor the direction and magnitude of the resulting plume, and are also located along the pipeline to monitor for possible leaks. A shore-based facility could provide power to the sensors and to get real-time data back and an autonomous underwater vehicle maps the near-field distribution of the plume. A towed undulating pumping system could monitor at distances of more than a few kilometres from the injection site. The towed system can provide much greater accuracy and precision on the measurements but will also be able to provide measurements over large areas in a relatively short period of time. Moored systems are used to monitor the plume between mapping cruises. These moorings have surface buoys and make daily transmissions back to the monitoring facility via satellite. The very far field distributions are monitored with hydrographic section cruises conducted every 2-5 years using standard discrete sampling approaches. These approaches provide the accuracy and precision required to detect the small CO_2 signals that add to background variations.

6.6.2 Monitoring amounts and distributions of materials released

6.6.2.1 Monitoring the near field

It appears that there is no serious impediment to verifying plant compliance with likely performance standards for flow through a pipe. Once CO_2 is discharged from the pipe then the specific

monitoring protocols will depend upon whether the plume is buoyant or sinking. Fixed location injections present fewer verification difficulties than do moving ship options.

For ocean injection from large point sources on land verifying compliance involves above ground inspection of facilities for verification of flow and that the CO_2 purity is consistent with environmental regulations (e.g., trace metal concentrations, etc.). For a power plant, flue gases could be monitored for flow rate and CO_2 partial pressure, thus allowing a full power plant carbon audit.

There are a variety of strategies to monitor release of CO_2 into the ocean from fixed locations. Brewer *et al.* (2005) observed a plume of CO_2 rich seawater emanating from a small-scale experimental release at 4 km depth with an array of *p*H and conductivity sensors. Measurements of ocean *p*H and current profiles at sufficiently high temporal resolution could be used to evaluate the rate of CO_2 release, local CO_2 accumulation and net transport away from the site (Sundfjord *et al.*, 2001). Undersea video cameras can monitor the point of release to observe CO_2 flow. The very large sound velocity contrast between liquid CO_2 (~300 m/s) and seawater (~1,500 m/s) offers the potential for very efficient monitoring of the liquid CO_2 phase using acoustical techniques (e.g., sonar).

The placement of CO_2 directly in a lake on the sea floor can be verified, and the quantity and loss rate determined, by a combination of acoustic, *p*H, and velocity measurements, and by direct inspection with underwater vehicles. Undersea vehicles, tethered or autonomous, could play a prominent role in monitoring and verification. Autonomous vehicles have been developed that can be programmed to efficiently follow a variety of complex trajectories over large areas (Simonetti, 1998), but accurate *p*H sensing in a rapidly changing pressure and temperature field has yet to be demonstrated. Deep-sea *p*H monitoring from tethered vehicles has been shown to be very precise (Brewer *et al.*, 2004), and these vehicles can routinely collect precisely located samples for later analysis.

6.6.2.2 Monitoring the far field

It will be possible to monitor the far field distributions of injected CO_2 using a combination of shipboard measurements and modelling approaches. The ability to identify *p*H plumes in the ocean has been well demonstrated (Figures 6.23). Current analytical techniques for measuring total CO_2 in the ocean are accurate to about ±0.05% (Johnson *et al.*, 1998). Thus, measurable changes could be seen with the addition of approximately 90 tons of CO_2/km^3. In other words, 1 $GtCO_2$ could be detected even if it were dispersed over 10^7 km^3 (i.e. a 5000 km by 2000 km by 1 km), if the dissolved inorganic carbon concentrations in the region were mapped out with high-density surveys before the injection began.

Figure 6.23. Measurements showing the ability to measure chemical effects of a natural CO_2 to plume. Profiles for pH were taken near the Axial Volcano at 46ºN 130ºW, in the ocean near Portland, Oregon, United States, in June 1999.

Variability in the upper ocean mixed layer would make it difficult to directly monitor small changes in CO_2 in waters shallower than the annual maximum mixed-layer depth. Seasonal mixing from the surface can extend as deep as 800 m in some places, but is less than 200 m in most regions of the ocean. Below the seasonal mixed layer, however, periodic ship-based surveys (every 2 to 5 years) could quantify the expansion of the injection plume.

We do not have a direct means of measuring the evasion to the atmosphere of carbon stored in the ocean. In most cases of practical interest the flux of stored CO_2 from the ocean to atmosphere will be small relatively to natural variability and the accuracy of our measurements. Operationally, it would be impossible to differentiate between carbon that has and has not interacted with the atmosphere. The use of prognostic models in evaluating the long-term fate of the injected CO_2 is critical for properly attributing the net storage from a particular site.

Given the natural background variability in ocean carbon concentrations, it would be extremely difficult, if not impossible, to measure CO_2 injected very far from the injection source. The attribution of a signal to a particular point source would become increasingly difficult if injection plumes from different locations begin to overlap and mix. In some parts of the ocean, it would be difficult to assign the elevation in CO_2 to intentional ocean storage as opposed to CO_2 from atmospheric absorption.

6.6.3 Approaches and technologies for monitoring environmental effects

Techniques now being used for field experiments could be used to monitor some near field consequences of direct CO_2 injection (Section 6.7). For example, researchers (Barry *et al.*, 2004, 2005; Carman *et al.*, 2004; Thistle *et al.*, 2005) have been developing experimental means for observing the consequences of elevated CO_2 on organisms in the deep ocean. However, such experiments and studies typically look for evidence of acute toxicity in a narrow range of species (Sato, 2004; Caulfield *et al.,* 1997; Adams *et al.*, 1997; Tamburri *et al.*, 2000). Sub-lethal effects have been studied by Kurihara *et al.* (2004). Process studies, surveys of biogeochemical tracers, and ocean bottom studies to could be used to evaluate changes in ecosystem structure and dynamics both before and after an injection.

It is less clear how best to monitor the health of broad reaches of the ocean interior (Sections 6.7.3 and 6.7.4). Ongoing long-term surveys of biogeochemical tracers and deep-sea biota could help to detect long-term changes in deep-sea ecology.

6.7. Environmental impacts, risks, and risk management

6.7.1 Introduction to biological impacts and risk

Overall, there is limited knowledge of deep-sea population and community structure and of deep-sea ecological interactions (Box 6.4). Thus, the sensitivities of deep ocean ecosystems to intentional carbon storage, and the effects on possibly unidentified goods and services that they may provide, remain largely unknown.

Box 6.4. Relevant background in biological oceanography.

Photosynthesis produces organic matter in the ocean almost exclusively in the upper 200 m where there is both light and nutrients (e.g., PO_4, NO_3, NH_4^+, Fe). Photosynthesis forms the base of a marine food chain that recycles much of the carbon and nutrients in the upper ocean. Some of this organic matter ultimately sinks to the deep ocean as particles and some of it is mixed into the deep ocean as dissolved organic matter. The flux of organic matter from the surface ocean provides most of the energy and nutrients to support the heterotrophic ecosystems of the deep ocean (Gage and Tyler, 1991). With the exception of the oxygen minimum zone and near volcanic CO_2 vents, most organisms living in the deep ocean live in low, more or less constant CO_2 levels.

At low latitudes, oxygen consumption and CO_2 release can produce a zone at around 1000 m

depth characterized by low O_2 and high CO_2 concentrations, known as the "oxygen minimum zone". Bacteria are the primary consumers of organic matter in the deep ocean; predominately, they obtain energy by consuming dissolved oxygen in reactions that oxidize organic carbon into CO_2. In the oxygen minimum layer seawater *p*H may be less than 7.7, roughly 0.5 *p*H units lower than average *p*H of natural surface waters (Figure 6.6).

At some locations near the sea floor, especially near submarine volcanic CO_2 sources, CO_2 concentrations can fluctuate greatly. Near deep-sea hydrothermal vents, CO_2 partial pressures (pCO_2, expressed as a ppm fraction of atmospheric pressure, equivalent to µatm) of up to 80,000 ppm have been observed (more than 100 times a typical value for deep-seawater). Typically, these vents are associated with fauna that have adapted over evolutionary time to these conditions; for example, tube worms can make use of high CO_2 levels for chemosynthetic CO_2 fixation in association with symbiotic bacteria (Childress *et al.*, 1993). High CO_2 levels (up to a pCO2 of 16,000 ppm; Knoll *et al.*, 1996) have been observed in ocean bottom waters and marine sediments where there are high rates organic matter oxidation and low rates of mixing with the overlying seawater. Under these conditions, high CO_2 concentrations are often accompanied by low O2 concentrations. Near the surface, respiratory fluxes in some relatively confined rock pools of the intertidal zone at night can produce high CO_2 levels. These patterns suggest that in some environments, organisms have evolved to tolerate relatively wide *p*H oscillations and/or low *p*H values.

Deep-sea ecosystems generally depend on sinking particles of organic carbon settling down through the water, made by photosynthesis near the ocean surface. Most species living in the deep-sea display very low metabolic rates (Childress, 1995), especially in oxygen minimum layers (Seibel *et al.*, 1997). Organisms living in the deep seawaters have adapted to the energy-limited environment by conserving energy stores and minimizing energy turnover. As a result of energy limitations and cold temperatures found in the deep sea, biological activities tend to be extremely low. For example, respiration rates of rat-tail fish are roughly 0.1% that of their shallow-water relatives. Community respiration declines exponentially with depth along the California margin, however, rapid turnover of large quantities of organic matter has been observed on the ocean floor (Mahaut *et al.*, 1995; Smith and Demopoulos, 2003). Thus, biological activity of some animals living on the deep sea floor can be as great as is found in relatives living on the sea floor in shallow waters.

Deep-sea ecosystems may take a long time to recover from disturbances that reduce population size. Organisms have adapted to the energy-limited environment of the deep-sea by limiting investment in reproduction, thus most deep-sea species produce few offspring. Deep-sea species tend to invest heavily in each of their eggs, making them large and rich in yolk to provide the offspring with the resources they will need for survival. Due to their low metabolic rates, deep-sea species tend to grow slowly and have much longer life spans than their upper-ocean cousins. For example, on the deep-sea floor, a bivalve less than 1 cm across can be more than 100 years old (Gage, 1991). This means that populations of deep-sea species will be more greatly affected by the loss of individual larvae than would upper ocean species. Upon disturbance, recolonization and community recovery in the deep ocean follows similar patterns as in shallow waters, however, on much longer time scales (several years compared to weeks or months in shallow waters, Smith and Demopoulos, 2003).

The numbers of organisms living on the sea floor per unit area decreases exponentially with depth, probably associated with the diminishing flux of food with depth. On the sea floor of the deepest ocean and of the upper ocean, the fauna can be dominated by a few species; between

2000 m and 3000 m depth ecosystems tend to have high species diversity with a low number of individuals, meaning that each species has a low population size (Snelgrove and Smith, 2002). The fauna living in the water column appear to be less diverse than that on the sea floor, probably due to the relative uniformity of vast volumes of water in the deep ocean.

Most ocean storage proposals seek to minimize the volume of water with high CO_2 concentrations either by diluting the CO_2 in a large volume of water or by isolating the CO_2 in a small volume (e.g., in CO_2 lakes). Nevertheless, if deployed widely, CO_2 injection strategies ultimately will produce large volumes of water with somewhat elevated CO_2 concentrations (Figure 6.15). Because large-amounts of relatively pure CO_2 have never been introduced to the deep ocean in a controlled experiment, conclusions about environmental risk must be based primarily on laboratory and small-scale in situ experiments, and extrapolation from these experiments using conceptual and mathematical models. Natural analogues (Box 6.5) can be relevant, but differ significantly from proposed ocean engineering projects.

Box 6.5. Natural analogues and earth history.

There are several examples of natural systems with strong CO_2 sources in the ocean, and fluid pools toxic to marine life, which may be examined to better understand possible physical and biological effects of active CO_2 injection.

Most natural environments that are heavily enriched in CO_2 (or toxic substances) host life forms that have adapted to these special conditions on evolutionary time scales. During Earth history much of the oceans may have hosted life forms specialized on elevated pCO_2, which are now extinct. This limits the use of natural analogues or Earth history to predict and generalize effects of CO_2 injection on most extant marine life.

- *Venting of carbon dioxide-rich fluids:* Hydrothermal vents, often associated with mid-ocean-ridge systems, often release CO_2 rich fluids into the ocean and can be used to study CO_2 behaviour and effects. For example, Sakai *et al.* (1990) observed buoyant hydrate forming fluids containing 86-91% CO_2 (with H_2S, and methane etc. making up the residual) released from the sea floor at 1335-1550m depth from a hydrothermal vent field. These fluids would be similar to a heavily contaminated industrial CO_2 source. These fluids arise from the reaction of seawater with acid and intermediate volcanic rocks at high temperature; they are released into seawater of 3.8°C. A buoyant hydrate-coated mass forms at the sea floor, which then floats upwards dissolving into the ocean water. Sea floor venting of aqueous fluids, rich in CO_2 and low in *p*H (3.5 - 4.4), is also to be found in some hydrothermal systems (Massoth *et al.*, 1989; Karl, 1995).

  Near volcanic vents, deep-sea ecosystems can be sustained by a geochemical input of chemical energy and CO_2. While there has been extensive investigation of these sites, and the plumes emanating from them, this has not yet been in the context of analogues for industrial CO_2 storage effects. Such an investigation would show how a fauna has evolved to adapt to a high-CO_2 environment; it would not show how biota adapted to normal ocean water would respond to increased CO_2 concentrations.
- *Deep saline brine pools:* The ocean floor is known to have a large number of highly saline brine pools that are anoxic and toxic to marine life. The salty brines freely dissolve, but mixing into the overlying ocean waters is impeded by the stable stratification imparted by the high density of the dissolving brines.

  The Red Sea contains many such brine pools (Degens and Ross, 1969; Anschutz *et al.*, 1999), some up to 60 km^2 in area, filled with high-temperature hyper-saline, anoxic, brine. Animals cannot survive in these conditions, and the heat and salt are transported across the brine-seawater interface form a plume into the surrounding bottom water. Hydrothermal sources resupply brine at the bottom of the brine pool (Anschutz and Blanc, 1996). The Gulf of Mexico

contains numerous brine pools. The largest known is the Orca Basin, where a 90 km^2 brine pool in 2250m water depth is fed by drainage from exposed salt deposits. The salt is toxic to life, but biogeochemical cycles operate at the interface with the overlying ocean (van Cappellen *et al.*, 1998). The Mediterranean also contains numerous large hypersaline basins (MEDRIFF Consortium, 1995).

Taken together these naturally occurring brine pools provide examples of vast volumes of soluble, dense, fluids, hostile to marine life, on the sea floor. The number, volume, and extent of these pools exceed those for scenarios for CO_2 lake formation yet considered. There has been little study of the impact of the plumes emanating from these sources. These could be examined to yield information that may be relevant to environmental impacts of a lake of CO_2 on the ocean floor.

- *Changes over geological time:* In certain times in Earth's geological past, the oceans may have contained more dissolved inorganic carbon and/or have had a lower *p*H.

  There is evidence of large-scale changes in calcifying organism distributions in the oceans in the geological record that may be related in changes in carbonate mineral saturation states in the surface ocean. For example, Barker and Elderfield (2002) demonstrated that glacial-interglacial changes in the shell weights of several species of planktonic foraminifera are negatively correlated with atmospheric CO_2 concentrations suggesting a causal relationship.

Cambrian CO_2 levels (i.e., about 500 myr ago) were as high as 5000 ppm and mean values decreased progressively thereafter (cf. Dudley, 1998; Berner, 2002). Two to three times higher than extant ocean calcium levels ensured that calcification of, for example, coral reefs was enabled in paleo-oceans despite high CO_2 levels (Arp *et al.*, 2001). High performance animal life appeared in the sea only after atmospheric CO_2 began to diminish; the success of these creatures may have depended on the reduction of atmospheric CO_2 levels (reviewed by Pörtner *et al.*, 2004, 2005). CO_2 is also thought to be a potential key factor in the late Permian/Triassic mass extinction, which affected corals, articulate brachiopods, bryozoans, and echinoderms to a larger extent than molluscs, arthropods and chordates (Knoll *et al.*, 1996; Berner, 2002; Bambach *et al.*, 2002). Pörtner *et al.* (2004) hypothesized that this may be due to the corrosive effect of CO_2 on heavily calcified skeletons. CO_2 excursions would have occurred in the context of large climate oscillations; effects of temperature oscillations, hypoxia events and CO_2 excursions likely contributed to extinctions (Pörtner *et al.*, 2005, see 6.7.3).

Compared to the surface, most of the deep sea is stable and varies little in its physiochemical factors over time (Box 6.4). The process of evolutionary selection has probably eliminated individuals apt to endure environmental perturbation. As a result, deep-sea organisms may be more sensitive to environmental disturbance than their shallow water cousins (Shirayama, 1997).

Ocean storage would occur deep in the ocean where there is virtually no light and photosynthesizing organisms are lacking; thus, the following discussion primarily addresses CO_2 effects on heterotrophic organisms, mostly animals. The diverse fauna that lives in the waters and sediments of the deep ocean can be affected by ocean CO_2 storage, leading to change in ecosystem composition and functioning. Thus, the effects of CO_2 need to be identified at the level of both the individual (physiological) and the ecosystem.

As described in Section 6.2, introduction of CO_2 into the ocean either directly into seawater or as a lake on the sea floor would result in changes in dissolved CO_2 near to and down current from a discharge point. Dissolving CO_2 in seawater (Box 6.1; Table 6.3) increases the partial pressure of CO_2 (pCO_2, expressed as a ppm fraction of atmospheric pressure, equivalent to µatm), causes decreased *p*H (more acidic) and decreased CO_3^{2-} concentrations (less saturated). This can lead to

dissolution of $CaCO_3$ in sediments or in shells of organisms. Bicarbonate (HCO_3^-) is then produced from carbonate (CO_3^{2-}).

Table 6.3. Relations between ΔpH, changes in pCO_2, and dissolved inorganic carbon concentration calculated for mean deep-sea conditions. Also shown are volumes of water needed to dilute 1 tCO_2 to the specified ΔpH, and the amount of CO_2 that, if uniformly distributed throughout the ocean, would produce this ΔpH.

The spatial extent of the waters with increased CO_2 content and decreased *p*H will depend on the amount of CO_2 released and the technology and approach used to introduce that CO_2 into the ocean. Table 6.3 shows the amount of seawater needed to dilute each tonne of CO_2 to a specified Δ*p*H reduction; further dilution would reduce the fraction of ocean at one Δ*p*H while increasing the volume of water experiencing a lesser Δ*p*H. Further examples indicating the spatial extent of ocean chemistry change from added CO_2 are represented in Figures 6.11, 6.12, 6.13, 6.14, and 6.15.

On evolutionary time scales most extant animal life has adapted to, on average, low ambient CO_2 levels. Accordingly, extant animal life may rely on these low pCO_2 values and it is unclear to what extent species would be able to adapt to permanently elevated CO_2 levels. Exposure to high CO_2 levels and extremely acidic water can cause acute mortality, but more limited shifts in CO_2, *p*H, and carbonate levels can be tolerated at least temporarily. Studies in shallow water organisms have identified a variety of physiological mechanisms by which changes in the chemical environment can affect fauna. These mechanisms should also apply to organisms living in the deep ocean. However, knowing physiological mechanisms alone does not enable full assessment of impacts at ecosystem levels. Long-term effects, for intervals greater than the duration of the reproduction cycle or the life span of an individual, may be overlooked yet may still drastically change an ecosystem.

Species living in the open ocean are exposed to low and relatively constant CO_2 levels, and thus may be sensitive to CO_2 exposure. In contrast, species dwelling in marine sediments, especially in the intertidal zone, are regularly exposed to CO_2 fluctuations and thus may be better adapted to high and variable CO_2 concentrations. Physiological mechanisms associated with CO_2 adaptation have been studied mostly in these organisms. They respond to elevated CO_2-concentrations by transiently diminishing energy turnover. However, such responses likely become detrimental during long-term exposure as reduced metabolism involves a reduction in physical activity, growth, and reproduction. Overall, marine invertebrates appear more sensitive than fish (Pörtner *et al.*, 2005).

CO_2 effects have been studied primarily in fish and invertebrates from shallow waters, although some of these cover wide depth ranges down to below 2000m or are adapted to cold temperatures (e.g. Langenbuch and Pörtner, 2003, 2004). Some *in situ* biological experiments used CO_2 in the deep ocean (See Box 6.6)

Box 6.6. In situ observations of the response of deep-sea biota to added CO_2.

In situ experiments concerning the sensitivity of deep and shallow-living marine biota to elevated carbon dioxide levels have been limited in scope. Significant CO_2 effects have been observed in experiments, consistent with the mechanisms of CO_2 action reported in Section 6.7.2. Some animals avoid CO_2 plumes, others do not.

Studies evaluating the behaviour and survival of deep-sea animals exposed to liquid CO_2 or to the CO_2 -rich seawater have been performed on the continental slope and rise off California. Experiments in which ~20-70 kg of liquid CO_2 were released in small corrals on the seafloor at

3600 m depth were used to measure the response of animals that came in contact with liquid CO_2, and to the dissolution plume emanating from CO_2 pools (Barry *et al.*, 2004). Larger bottom-living animals collected from the seafloor were held in cages and placed at distances of 1-50 m from CO_2 pools. In addition, organisms living in the sediment were collected at a range of distances from CO_2 pools, both before CO_2 release and 1-3 months later.

The response of animals to direct contact with liquid CO_2 varied among species. Sea cucumbers (holothurians like Scotoplanes sp.) and brittle stars (ophiuroids, unidentified species) died immediately after contact with liquid CO_2 (Barry *et al.*, 2005). A few individuals (<5 individuals) of deep-sea fish (grenadiers, *Coryphaenoides armatus*) that approached CO_2 pools and made contact with the fluid turned immediately and swam out of view. Other deep-sea experiments (Tamburri *et al.* 2000) evaluating the behavioural response of animals to a saturated CO_2 / seawater solution have shown that some scavenger species (deep-sea hagfishes) will not avoid acidic, CO_2-rich seawater, if chemical cues from decaying bait are also present. In fact, hagfish would maintain contact with the CO_2 -rich / bait-scented plume long enough to be apparently "narcotized" by the CO_2.
Survival rates of abyssal animals exposed to CO_2 dissolution plumes in these experiments varied with the range of *p*H perturbation and the distance from the CO_2 source. Abyssal animals held in cages or inhabiting sediments that were near (<1 m) CO_2 pools, and which were exposed episodically to large *p*H reduction (1-1.5 *p*H units) experienced high rates of mortality (>80%). Animals affected included small (meio-)fauna (flagellates, amoebae, nematodes; Barry *et al.*, 2004) and larger (macro and mega-)fauna (Ampeliscid amphipod species, invertebrates like holothurians, echinoids, and fishes like macrourids). Other fish like eelpout (zoarcids), however, all survived month-long exposure to episodic *p*H shifts of ~-1.0 *p*H units. Animals held further (3-10 m) from CO_2 pools were exposed to mild episodic *p*H reductions (~0.1 – 0.2 *p*H units) exhibited mortality rates were (~20-50%) higher than at control sites (Barry *et al.*, 2005).

It is unknown whether mortality was caused primarily by short-term exposure to large *p*H / CO_2 shifts or by chronic, milder *p*H perturbations. Tidal variation in current direction resulted in a highly variable exposure to *p*H perturbations with the most intense exposure to dissolution plumes when the current was flowing directly toward the study animals. During other tidal periods, there was often no *p*H reduction, increasing the difficulty of interpreting these experiments.

Three controlled in situ experiments were carried out at 2000 m in the Kumano Trough using a specially designed chamber (Figure 6.24; Ishida *et al.* 2004) to address the impact of a 5,000 and 20,000 ppm rise in pCO_2 (with *p*H resulting at 6.8 and 6.3) on the abundance and diversity of bacteria and of small animals (nano- and meiobenthos). Significant impacts of elevated pCO_2 on meiobenthic organisms could not be found except for one case where the abundance of foraminifera decreased significantly within 3 days under 20,000 ppm. The abundance of nanobenthos decreased significantly in most cases, whereas the abundance of bacteria increased under 20,000 ppm (Figure 6.25).

Figure 6.24. Experimental chamber going to the sea floor. The bottom part houses a chamber that penetrates into the sediment. The top part houses electronics, pumps, valves, and water bags, that are used to control the CO_2 concentration inside the chamber, and to sample seawater in the chamber at designated times. At the time of recovery, the bottom of the chamber is closed, weights are released, and the system come back to the surface of the ocean using buoyancy provided by the glass bulbs (yellow structures around the top).

Figure 6.25. Preliminary investigations into the change of bacteria, nanobenthos and meiobenthos abundance after exposure to 20,000 and 5,000 ppm CO_2 for 77 to 375 hr during three experiments carried out at 2,000 m deep in Nankai Trough, North Western Pacific. Error bars represent one standard deviation (Ishida et al. 2004).

In situ studies of short-term effects of elevated CO_2 concentrations on deep-sea megafauna have been conducted using CO_2 released naturally from the Loihi Seamount (Hawaii) at depths of 1200 to 1300 m (Vetter and Smith, 2005). A submersible was used to manipulate baited traps and bait parcels in Loihi's CO_2 plume to explore the effects of elevated CO_2 on typical deep-sea scavengers. Vent-specialist shrimp were attracted to the bait and proved to be pre-adapted to the high CO_2 levels found close to volcanic vents. Free swimming, amphipods, synaphobranchid eels, and hexanchid sharks avoided open bait parcels placed in the CO_2 plumes

6.7.2 Physiological effects of CO_2

6.7.2.1 Effects of CO_2 on cold-blooded water breathing animals

Hypercapnia is the condition attained when an organism (or part thereof) is surrounded by high concentrations of CO_2. Under these conditions, CO_2 enters the organisms by diffusion across body and especially respiratory surfaces and equilibrates with all body compartments. This internal accumulation of CO_2 will be responsible for most of the effects observed in animals (reviewed by Pörtner and Reipschläger, 1996, Seibel and Walsh, 2001, Ishimatsu *et al.*, 2004, 2005; Pörtner *et al.*, 2004, 2005). Respiratory distress, narcosis, and mortality are the most obvious short term effects at high CO_2 concentrations, but lower concentrations may have important effects on longer time scales. The CO_2 level to which an organism has acclimated may affect its acute critical CO_2 thresholds, however, the capacity to acclimate has not been investigated to date.

6.7.2.2 Effects of CO_2 versus p*H*

Typically, tolerance limits to CO_2 have been characterized by changes in ocean *p*H or pCO_2 (cf. Shirayama, 1995; Auerbach *et al.*, 1997). However, changes in molecular CO_2, carbonate, and bicarbonate concentrations in ambient water and body fluids may each have specific effects on marine organisms (Pörtner and Reipschläger, 1996). In water breathers like fish or invertebrates CO_2 entry causes immediate disturbances in acid-base status, which need to be compensated for by ion exchange mechanisms. The acute effect of CO_2 accumulation is more severe than that of the reduction in *p*H or carbonate-ion concentrations. For example, fish larvae are more sensitive to low *p*H and high CO_2 than low *p*H and low CO_2 (achieved by addition of HCl with pCO_2 levels kept low by aeration; Ishimatsu *et al.*, 2004).

CO_2 added to seawater will change the hydrogen-ion concentration (*p*H); this change in hydrogen-ion concentration may affect marine life through mechanisms that do not directly involve CO_2. Studies of effects of lowered *p*H (without concomitant CO_2 accumulation) on aquatic organisms have a long history, with an emphasis on freshwater organisms (Wolff *et al.*, 1988). Observed consequences of lowered water *p*H (at constant pCO_2) include changes in production/productivity patterns in algal and heterotrophic bacterial species, changes in biological calcification/ decalcification processes, and acute and sub-acute metabolic impacts on zooplankton species, ocean bottom species, and fish. Furthermore, changes in the *p*H of marine environments affect: (1) the carbonate system, (2) nitrification (Huesemann *et al.*, 2002) and speciation of nutrients such as phosphate, silicate and ammonia (Zeebe and Wolf-Gladrow, 2001), and (3) speciation and uptake of essential and toxic trace elements. Observations and chemical calculations show that low *p*H

conditions generally decrease the association of metals with particles and increase the proportion of biologically available free metals (Sadiq, 1992; Salomons and Forstner, 1984). Aquatic invertebrates take up both essential and non-essential metals, but final body concentrations of metals vary widely across invertebrates. In the case of many trace metals, enhanced bioavailability is likely to have toxicological implications, since free forms of metals are of the greatest toxicological significance (Rainbow, 2002).

6.7.2.3 Acute CO_2 sensitivity: oxygen transport in squid and fish

CO_2 accumulation and uptake can cause anaesthesia in many animal groups. This has been observed in deep-sea animals close to hydrothermal vents or experimental CO_2 pools. A narcotic effect of high, non-determined CO_2 levels was observed in deep-sea hagfish after CO_2 exposure in situ (Tamburri *et al.*, 2000). Prior to anaesthesia high CO_2 levels can exert rapid effects on oxygen transport processes and thereby contribute to acute CO_2 effects including early mortality.

Among invertebrates, this type of CO_2 sensitivity may be highest in highly complex, high performance organisms like squid (reviewed by Pörtner *et al.*, 2004). Blue-blooded squid do not possess red blood cells (erythrocytes) to protect their extracellular blood pigment (haemocyanin) from excessive *p*H fluctuations. Acute CO_2 exposure causes acidification of the blood, will hamper oxygen uptake and binding at the gills and reduce the amount of oxygen carried in the blood, limiting performance and at high concentrations could cause death. Less oxygen is bound to haemocyanin in squid than is bound to haemoglobin in bony fish (teleosts). Jet-propulsion swimming of squid demands a lot of oxygen. Oxygen supply is supported by enhanced oxygen binding with rising blood *p*H (and reduced binding of oxygen with falling pH - a large Bohr effect[3]). Maximization of oxygen transport in squid thus occurs by means of extracellular pH oscillations between arterial and venous blood. Therefore, finely controlled extracellular pH changes are important for oxygen transport. At high CO_2 concentrations, animals can asphyxiate because the blood cannot transport enough oxygen to support metabolic functions. In the most active open ocean squid (*Illex illecebrosus*), model calculations predict acute lethal effects with a rise in pCO_2 by 6500 ppm and a 0.25 unit drop in blood *p*H. However, acute CO_2 sensitivity varies between squid species. The less active coastal squid (*Loligo pealei*) is less sensitive to added CO_2.

In comparison to squid and other invertebrates, fish (teleosts) appear to be less sensitive to added CO_2, probably due to their lower metabolic rate, presence of red blood cells (erythrocytes containing haemoglobin) to carry oxygen, existence of a venous oxygen reserve, tighter epithelia, and more efficient acid-base regulation. Thus, adult teleosts (bony fish) exhibit a larger degree of independence from ambient CO_2. A number of tested shallow-water fishes have shown relatively high tolerance to added CO_2, with short-term lethal limits of adult fish at a pCO_2 of about 50,000 to 70,000 ppm. European eels (*Anguilla anguilla*) displayed exceptional tolerance of acute hypercapnia up to 104,000 ppm (for review see Ishimatsu *et al.*, 2004, Pörtner *et al.*, 2004). The cause of death in fish involves a depression of cardiac functions followed by a collapse of oxygen delivery to tissues (Ishimatsu *et al.*, 2004). With mean lethal CO_2 levels of 13,000 to 28,000 ppm, juveniles are more sensitive to acute CO_2 stress than adults. In all of these cases, the immediate cause of death appears to be entry of CO_2 into the organism (and not primarily some other *p*H-mediated effect).

[3] "The Bohr Effect is an adaptation in animals to release oxygen in the oxygen starved tissues in capillaries where respiratory carbon dioxide lowers blood *p*H. When blood *p*H decreases, the ability of the blood pigment to bind to oxygen decreases. This process helps the release of oxygen in the oxygen-poor environment of the tissues." modified after *ISCID Encyclopedia of Science and Philosophy*. 2004. International Society for Complexity, Information, and Design. 12 October 2004 <http://www.iscid.org/encyclopedia/Bohr_Effect>.

Fish may be able to avoid contact to high CO_2 exposure because they possess highly sensitive CO_2 receptors that could be involved in behavioural responses to elevated CO_2 levels (Yamashita *et al.*, 1989). However, not all animals avoid low pH and high concentrations of CO_2; they may actively swim into CO_2-rich regions that carry the odour of potential food (e.g. bait; Tamburri *et al.*, 2000, Box 6.6).

Direct effects of dissolved CO_2 on diving marine air breathers (mammals, turtles) can likely be excluded since they possess higher pCO_2 values in their body fluids than water breathers and gas exchange is minimized during diving. They may nonetheless be indirectly affected through potential CO_2 effects on the food chain (see 6.7.5).

6.7.2.4 Deep vs. shallow acute CO_2 sensitivity

Deep-sea organisms may be less sensitive to high CO_2 levels than their cousins in surface waters, but this is controversial. Fish (and cephalopods) lead a sluggish mode of life with reduced oxygen demand at depths below 300 to 400 m. Metabolic activity of pelagic animals, including fishes and cephalopods, generally decreases with depth (Childress, 1995; Seibel *et al.*, 1997). However, Seibel and Walsh (2001) postulated that deep-sea animals would experience serious problems in oxygen supply under conditions of increased CO_2 concentrations. They refer to midwater organisms that may not be representative of deep-sea fauna; as residents of so called 'oxygen minimum layers' they have special adaptations for efficient extraction of oxygen from low-oxygen waters (Sanders and Childress, 1990; Childress and Seibel, 1998).

6.7.2.5 Long-term CO_2 sensitivity

Long- term impacts of elevated CO_2 concentrations are more pronounced on early developmental than on adult stages of marine invertebrates and fish. Long-term depression of physiological rates may, over time scales of several months, contribute to enhanced mortality rates in a population (Shirayama, 2002, Langenbuch and Pörtner, 2004). Prediction of future changes in ecosystem dynamics and structure and functioning therefore requires data on sub-lethal effects over the entire life history of organisms.

The mechanisms limiting performance and long term survival under moderately elevated CO_2 levels are even less clear than those causing acute mortality. However, they appear more important since they may generate impacts in larger ocean volumes during widespread distribution of CO_2 at moderate levels on long time scales. In animals relying on calcareous exoskeletons physical damage may occur under permanent CO_2 exposure through reduced calcification and even dissolution of the skeleton; however, effects of CO_2 on calcification processes in the deep ocean have not been studied to date. Numerous studies have demonstrated the sensitivity of calcifying organisms living in surface waters to elevated CO_2 levels on longer time scales (Gattuso *et al.* 1999, Reynaud *et al.*, 2003, Feeley *et al.*, 2004 and refs. therein). At least a dozen laboratory- and field-based studies of corals and coralline algae have suggested reductions in calcification rates by 15-85% with a doubling of CO_2 (to 560 ppm) from pre-industrial levels. Shirayama (2002) demonstrated that increases in dissolved CO_2 levels to 560 ppm causes a reduction in growth rate and survival of shelled animals like echinoderms and gastropods. These findings indicate that previous atmospheric CO_2 accumulation may already be affecting the growth of calcifying organisms, with the potential for large-scale changes in surface-ocean ecosystem structure. Due to atmospheric CO_2 accumulation global calcification rates could decrease by 50% over the next century (Zondervan *et al.*, 2001), and there could be significant shifts in global biogeochemical cycles. Despite the potential importance of biogeochemical feedback induced by global change, our understanding of these processes is still in its infancy even in surface waters (Riebesell, 2004). Much less can be said about potential ecosystem shifts in the deep sea (Omori *et al.*, 1998).

Long-term effects of CO_2 elevations identified in individual animal species affects processes in addition to calcification (reviewed by Ishimatsu *et al.*, 2004, Pörtner and Reipschläger, 1996, Pörtner *et al.*, 2004, 2005). In these cases, CO_2 entry into the organism as well as decreased water *p*H values are likely effective. Major effects occur through a disturbance in acid-base regulation of several body compartments. Falling *p*H values result, which affect many metabolic functions, since enzymes and ion transporters are only active over a narrow *p*H range. *p*H decreases from CO_2 accumulation are counteracted over time by an accumulation of bicarbonate anions in the affected body compartments (Heisler, 1986; Wheatly and Henry, 1992, Pörtner *et al.*, 1998; Ishimatsu *et al.* 2004) but compensation is not always complete. Acid-base relevant ion transfer may disturb osmoregulation due to the required uptake of appropriate counter ions, which leads to an additional NaCl load of up to 10% in marine fish in high-CO_2 environments (Evans, 1984; Ishimatsu *et al.*, 2004). Long-term disturbances in ion equilibria could be involved in mortality of fish over long time scales despite more or less complete compensation of acidification.

Elevated CO_2 levels may cause a depression of aerobic energy metabolism, due to incomplete compensation of the acidosis, as observed in several invertebrate examples (reviewed by Pörtner *et al.* 2004, 2005). In one model organism, the peanut worm *Sipunculus nudus*, high CO_2 levels caused metabolic depression by up to 35% at 20,000 ppm pCO_2. A central nervous mechanism also contributed indicated by the accumulation of adenosine in the nervous tissue under 10,000 ppm pCO_2. Adenosine caused metabolic depression linked to reduced ventilatory activity even more so when high CO_2 was combined with oxygen deficiency (anoxia; Lutz and Nilsson, 1997). Studies addressing the specific role of adenosine or other neurotransmitters at lower CO_2 levels or in marine fishes during hypercapnia are not yet available.

The depression of metabolism observed under high CO_2 concentrations in marine invertebrates also includes inhibition of protein synthesis — a process that is fundamental to growth and reproduction. A CO_2 induced reduction water *p*H to 7.3 caused a 55 % reduction in growth of Mediterranean mussels (Michaelidis *et al.* 2005; for review see Pörtner *et al.* 2004, 2005). Fish may also grow slowly in high CO_2 waters. Reduced growth was observed in juvenile white sturgeon (Crocker and Cech, 1996). In this case, the stimulation of ventilation and the associated increase in oxygen consumption indicated a shift in energy budget towards maintenance metabolism, which occurred at the expense of growth. This effect was associated with reductions in foraging activity. A harmful influence of CO_2 on reproductive performance was found in two species of marine copepods (*Acartia steuri, Acartia erythrea*) and sea urchins (*Hemicentrotus purcherrimus, Echinometra mathaei*). While survival rates of adult copepods were not affected during 8 days at pCO_2 up to 10,000 ppm, egg production and hatching rates of eggs were significantly reduced concomitant to an increased mortality of young-stage larvae seen at water *p*H 7.0 (Kurihara *et al.*, 2004). In both sea urchin species tested, fertilization rates decreased with pCO_2 rising above1000 ppm (below water *p*H 7.6; Kurihara *et al.*, 2004). Hatching and survival of fish larvae also declined with water pCO_2 and exposure time in all examined species (Ishimatsu *et al.*, 2004).

6.7.3 From physiological mechanisms to ecosystems

CO_2 effects propagate from molecules via cells and tissues to whole animals and ecosystems (Figure 6.26; Table 6.4). Organisms are affected by chemistry changes that modulate crucial physiological functions. The success of a species can depend on effects on the most sensitive stages of its life cycle (e.g., egg, larvae, adult). Effects on molecules, cells, and tissues thus integrate into whole animal effects (Pörtner *et al.*, 2004) affecting growth, behaviour, reproduction, and development of eggs and larvae. These processes then determine the ecological success (fitness) of a species, which can also depend on complex interaction among species. Differential effects of

chemistry changes on the various species thus affect the entire ecosystem. Studies of CO_2 susceptibility and affected mechanisms in individual species (Figure 6.26) support development of a cause and effect understanding for an entire ecosystem's response to changes in ocean chemistry, but need to be complemented by field studies of ecosystem consequences.

Table 6.4. Physiological and ecological processes affected by CO_2 (note that listed effects on phytoplankton are not relevant in the deep sea, but may become operative during large scale mixing of CO_2). Based on reviews by Heisler, 1986, Wheatly and Henry, 1992, Claiborne et al., 2002, Langdon et al., 2003 Shirayama, 2002, Kurihara et al., 2004, Ishimatsu et al., 2004, 2005, Pörtner et al. 2004, 2005, Riebesell, 2004, Feeley et al., 2004 and references therein.

Figure 6.26. Effects of added CO_2 at the scale of molecule to organism and associated changes in proton (H^+), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) levels in a generalized and simplified marine invertebrate or fish. The blue region on top refers to open water; the tan region represents the organism. Generalized cellular processes are depicted on the left and occur in various tissues like brain, heart or muscle; depression of these processes has consequences (depicted on the right and top). Under CO_2 stress, whole animal functions like growth, behaviours, or reproduction are depressed (adopted from Pörtner et al., 2005, - or + denotes a depression or stimulation of the respective function). Black arrows reflect diffusive movement of CO_2 between compartments; red arrows reflect effective factors, CO_2, H^+, HCO_3^- that modulate functions. Shaded areas indicate processes relevant for growth and energy budget.

Tolerance thresholds likely vary between species and phyla, but still await quantification for most organisms. Due to differential sensitivities among and within organisms, a continuum of impacts on ecosystems is more likely than the existence of a well-defined threshold beyond which CO_2 cannot be tolerated. Many species may be able to tolerate transient CO_2 fluctuations but may not be able to settle and thrive in areas where CO_2 remains permanently elevated. At concentrations that do not cause acute mortality, limited tolerance may include reduced capacities of higher functions, i.e. added CO_2 could reduce the capacity of growth and reproduction, or hamper resistance to infection (Burnett 1997). It could also reduce the capacity to attack or escape predation, which would have consequences for the organism's food supply and thus overall fitness with consequences for the rest of the ecosystem.

Complex organisms like animals proved to be more sensitive to changing environmental conditions like temperature extremes than are simpler, especially unicellular, organisms (Pörtner, 2002); it is not known whether animals are also more sensitive to extremes in CO_2. CO_2 affects many physiological mechanisms that are also affected by temperature and hypoxia (Figure 6.26). Challenges presented by added CO_2 could lower long-term resistance to temperature extremes and thus narrow zoogeographical distribution ranges of affected species (Reynaud *et al.*, 2003, Pörtner *et al.*, 2005).

At the ecosystem level, few studies carried out in surface oceans report that species may benefit under elevated CO_2 levels. Riebesell (2004) summarized observations in surface ocean mesocosms under glacial (190 ppm) and increased CO_2 concentrations (790 ppm). High CO_2 concentrations caused higher net community production of phytoplankton. Diatoms dominated under glacial and elevated CO_2 conditions, whereas *Emiliania huxleyi* dominated under present CO_2 conditions. This example illustrates how species that are less sensitive to added CO_2 could become dominant in a high CO_2 environment, in this case due to stimulation of photosynthesis in resource limited phytoplankton species (Riebesell 2004). These conclusions have limited applicability to the deep

sea, where animals and bacteria dominate. In animals, most processes are expected to be depressed by high CO_2 and low *p*H levels (Table 6.4).

6.7.4 Biological consequences for water column release scenarios

Overall, extrapolation from knowledge mostly available for surface oceans indicates that acute CO_2 effects (e.g. narcosis, mortality) will only occur in areas where pCO_2 plumes reach significantly above 5000 ppm of atmospheric pressure (in the most sensitive squid) or above 13,000 or 40,000 ppm for juvenile or adult fish, respectively. Such effects are thus expected at CO_2 increases with $\Delta pH < -1.0$ for squid (according to the example presented in Figure 6.12, a towed pipe could avoid *p*H changes of this magnitude; however, a fixed pipe without design optimization would produce a volume of several km^3 with this *p*H change for an injection rate of 100 kg s^{-1}). Depending on the scale of injection such immediate effects may thus be chosen to be confined to a small region of the ocean (Figures 6.13 and 6.14).

Available knowledge of CO_2 effects and underlying mechanisms indicate that effects on marine fauna and their ecosystems will likely set in during long-term exposure to pCO_2 of more than 400 to 500 ppm or associated moderate *p*H changes (by ~0.1 – 0.3 units), primarily in marine invertebrates (Pörtner *et al.* 2005) and, possibly, unicellular organisms. For injection at a rate of 0.37 $GtCO_2$ yr^{-1} for 100 years (Figure 6.14), such critical *p*H shifts would occur in less than 1 % of the total ocean volume by the end of this period. However, baseline *p*H shifts by 0.2 to 0.4 *p*H-units expected from the WRE550 stabilisation scenario already reach that magnitude of change. Additional long-term repeated large-scale global injection of 10 % of the CO_2 originating from 18,000 $GtCO_2$ fossil fuel would cause an extension of these *p*H shifts from the surface ocean to significantly larger (deeper) fractions of the ocean by 2100 to 2300 (Figure 6.15). Finally, large-scale ocean disposal of all of the CO_2 would lead to *p*H decreases of more than 0.3 and associated long term effects in most of the ocean. Expected effects will include a reduction in the productivity of calcifying organisms leading to higher ratios of non-calcifiers over calcifiers (Pörtner *et al.*, 2005). Reduced capacities for growth, productivity, behaviours, and reduced life span imply a reduction in population densities and productivities of some species, if not reduced biodiversity. Food chain length and composition may be reduced associated with reduced food availability for high trophic levels. This may diminish resources for local or global fisheries. The suggested scenarios of functional depression also include a CO_2 induced reduction in tolerance to thermal extremes, which may go hand in hand with reduced distribution ranges as well as enhanced geographical distribution shifts. All of these expectations result from extrapolations of current physiological and ecological knowledge and require verification in experimental field studies. The capacity of ecosystems to compensate or adjust to such CO_2 induced shifts is also unknown; continued research efforts could identify critical mechanisms, titrate/quantify (lab and field) scenarios and address the potential for adaptation on evolutionary timescales.

6.7.5 Biological consequences associated with CO_2 lakes

Strategies that release liquid CO_2 close to the sea floor will be affecting two ecosystems: the ecosystem living on the seafloor, and deep-sea ecosystem living in the overlying water. Storage as a topographically confined "CO_2 lake" would limit immediate large scale effects of CO_2 addition, but result in the mortality of most organisms under the lake that are not able to flee and of organisms that wander into the lake. CO_2 will dissolve from the lake into the bottom water, and this will disperse around the lake, with effects similar to direct release of CO_2 into the overlying water. According to the scenarios depicted in Figures 6.11 and 6.12 for CO_2 releases near the sea floor, *p*H reductions expected in the near field are well within the scope of those expected to exert significant effect on marine biota, depending on the length of exposure**.**

6.7.6 Contaminants in CO_2 streams

The injection of large quantities of CO_2 into the deep ocean will itself be the topic of environmental concern, so the matter of possible small quantities of contaminants in the injected material is of additional but secondary concern. In general there are already stringent limits on contaminants in CO_2 streams due to human population concerns, and technical pipeline considerations. The setting of any additional limits for ocean disposal cannot be addressed with any certainty at this time.

There are prohibitions in general against ocean disposal; historical concerns have generally focused on heavy metals, petroleum products, and toxic industrial chemicals and their breakdown products.

A common contaminant in CO_2 streams is H_2S. There are very large sources of H_2S naturally occurring in the ocean: many marine sediments are anoxic and contain large quantities of sulphides; some large ocean basins (the Black Sea, the Cariaco Trench etc.) are anoxic and sulphidic. As a result ocean ecosystems that have adapted to deal with sulphide and sulphur-oxidizing bacteria are common throughout the world ocean. Nonetheless the presence of H_2S in the disposal stream would result in a lowering of local dissolved oxygen levels, and have impact on respiration and performance of higher marine organisms.

6.7.7 Risk management

There is no peer-reviewed literature directly addressing risk management for intentional ocean carbon storage; however, there have been risk management studies related to other uses of the ocean. Oceanic CO_2 release carries no expectation of risk of catastrophic atmospheric degassing such as occurred at Lake Nyos (Box 6.7). Risks associated with transporting CO_2 to depth are discussed in Chapter 4 (Transportation).

Box 6.7. Lake Nyos and deep-sea carbon storage.

About 2 million tonnes of CO_2 gas produced by volcanic activity were released in one night in 1986 by Lake Nyos, Cameroon, causing the death of at least 1700 people (Kling *et al.*, 1994). Could CO_2 released in the deep sea produce similar catastrophic release at the ocean surface?

Such a catastrophic degassing involves the conversion of dissolved CO_2 into the gas phase. In the gas phase, CO_2 is buoyant and rises rapidly, entraining the surrounding water into the rising plume. As the water rises, CO_2 bubbles form more readily. These processes can result in the rapid release of CO_2 that has accumulated in the lake over a prolonged period of magmatic activity.

Bubbles of CO_2 gas can form in seawater only shallower than about 500 m depth when the partial pressure of CO_2 in seawater exceeds the ambient total pressure. Most release schemes envision CO_2 release deeper than this depth. CO_2 released below 3000 m would tend to sink and then dissolve into the surrounding seawater. CO_2 droplets released more shallowly generally dissolve within a few 100 vertical meters of release.

The resulting waters are too dilute in CO_2 to produce partial CO_2 pressures exceeding total ambient pressure, thus CO_2 bubbles would not form. Nevertheless, if somehow large volumes of liquid CO_2 were suddenly transported above the liquid-gas phase boundary, there is a possibility of a self-accelerating regime of fluid motion that could lead to rapid degassing at the surface. The disaster at Lake Nyos was exacerbated because the volcanic crater confined the CO_2 released by the lake; the open ocean surface does not provide such topographic confinement.Thus, there is no known mechanism that could produce an unstable volume of water containing 2 million tCO_2 at depths shallower than 500 m, and thus no mechanism known by which ocean carbon storage could produce

a disaster like that at Lake Nyos.

It may be possible to recover liquid CO_2 from a lake on the ocean floor. The potential reversibility of the production of CO_2-lakes might be considered a factor that diminishes risk associated with this option.

6.7.8 Social aspects; public and stakeholder perception

The study of public perceptions and perceived acceptability of intentional CO_2 storage in the ocean is at an early stage and comprises only a handful of studies (Curry *et al.*, 2004; Gough *et al.*, 2002; Itaoka *et al.*, 2004; Palmgren *et al.*, 2004) Issues crosscutting public perception of both geologic and ocean storage are discussed in Section 5.8.5.

All studies published to date addressing ocean storage have shown that the public is largely uninformed about ocean carbon storage and thus holds no well-developed opinion. There is very little awareness among the public regarding intentional or unintentional ocean carbon storage. For example, Curry *et al.* (2004) found that the public was largely unaware of the role of the oceans in absorbing anthropogenic carbon dioxide released to the atmosphere. In the few relevant studies conducted thus far, the public has expressed more reservations regarding ocean carbon CO_2 storage than for geologic CO_2 storage.

Education can affect the acceptance of ocean storage options. In a study conducted in Tokyo and Sapporo, Japan (Iatoka et al, 2004), when members of the public, after receiving some basic information, were asked to rate ocean and geologic storage options on a 1 to 5 scale (1 = no, 5 = yes) the mean rating for dilution-type ocean storage was 2.24, lake-type ocean storage was rated at 2.47, onshore geologic storage was rated at 2.57, and offshore geologic storage was rated at 2.75. After receiving additional information from researchers, the mean rating for dilution-type and lake-type ocean storage increased to 2.42 and 2.72, respectively, while the mean ratings for onshore and offshore geologic storage increased to 2.65 and 2.82, respectively. In a similar conducted study in Pittsburgh, USA, Palmgren *et al.* (2004) found that when asked to rate ocean and geologic storage on a 1 to 7 scale (1 = completely oppose, 7 = completely favour) respondents' mean rating was about 3.2 for ocean storage and about 3.5 for geologic storage. After receiving information selected by the researchers, the respondents changed their ratings to about 2.4 for ocean storage and 3.0 for geologic storage. Thus, in the Itaoka *et al.* (2004) study the information provided by the researchers increased the acceptance of all options considered whereas in the Study of Palmgren *et al.* (2004) the information provided by the researchers decreased the acceptance of all options considered. The differences could be due to many causes, nevertheless, they suggest that the way information is provided by researchers could affect whether the added information increases or decreases the acceptability of ocean storage options.

Gough *et al.* (2002) reported results from discussions of carbon storage from two unrepresentative focus groups comprising a total of 19 people. These focus groups also preferred geologic storage to ocean storage; this preference appeared to be based, "not primarily upon concerns for the deep-sea ecological environment", but on "the lack of a visible barrier to prevent CO_2 escaping" from the oceans. Gough *et al.* (2002) notes that "significant opposition" developed around a proposed ocean CO_2 release experiment in the Pacific Ocean (see Section 6.2.1.2).

6.8. Legal issues

6.8.1 International law

Please refer to Sections 5.8.1.1 (*Sources and nature of international obligations*) and 5.8.1.2 (*Key issues in the application of the treaties to* CO_2 *storage*) for the general position of both geological and ocean storage of CO_2 under international law. It is necessary to look at and interpret the primary sources, the treaty provisions themselves, to determine the permissibility or otherwise of ocean storage. Some secondary sources, principally the 2004 OSPAR Jurists Linguists' paper containing the States Parties' interpretation of the Convention (considered in detail in Section 5.8.1.3) and conference papers prepared for the IEA workshop in 1996, contain their authors' individual interpretations of the treaties.

McCullagh (1996) considered the international legal control of ocean storage, and found that, whilst the UN Framework Convention on Climate Change (UNFCCC) encourages the use of the oceans as a reservoir for CO_2, the UN Convention on the Law of the Sea (UNCLOS) is ambiguous in its application to ocean storage. Whilst ocean storage will reduce CO_2 emissions and combat climate change, to constitute an active use of sinks and reservoirs as required by the UNFCCC, ocean storage would need to be the most cost-effective mitigation option. As for UNCLOS, it is unclear whether ocean storage will be allowable in all areas of the ocean, but provisions on protecting and preserving the marine environment will be applicable if CO_2 is deemed to be "pollution" under the Convention (which will be so as the large quantities of CO_2 introduced is likely to cause harm to living marine resources). In fulfilling their obligation to prevent, reduce and control pollution of the marine environment, States must act so as not to transfer damage or hazards from one area to another or transform one type of pollution into another, a requirement that could be relied upon by proponents and opponents alike.

Churchill (1996) too focuses on UNCLOS in his assessment of the international legal issues, and finds that the consent of the coastal State would be required if ocean storage occurred in that State's territorial sea (up to12 miles from the coast). In that State's Exclusive Economic Zone (up to 200 miles), the storage of CO_2 via a vessel or platform (assuming it constituted "dumping" under the Convention) would again require the consent of that State, its discretion being limited by its obligation to have due regard to the rights and duties of other States in the Exclusive Economic Zone under the Convention, other treaty obligations (London and OSPAR) and the Convention's general duty on Parties not to cause damage by pollution to other States' territories or areas beyond its national jurisdiction. He finds that it is uncertain whether the definition of "dumping" would apply to use of a pipeline system from land for ocean storage, but, in any event, concludes that the discharge of CO_2 from a pipeline will, in many circumstances, constitute pollution and thus require the coastal State to prevent, reduce and control such pollution from land based sources. But ocean storage by a pipeline from land into the Exclusive Economic Zone will not fall within the rights of a coastal or any other State and any conflict between them will be resolved on the basis of equity and in the light of all the relevant circumstances, taking into account the respective importance of the interests involved to the parties as well as to the international community as a whole. He finds that coastal States do have the power to regulate and control research in their Exclusive Economic Zones, although such consent is not normally to be withheld except in some cases.

As for the permissibility of discharge of CO_2 into the high seas (the area beyond the Exclusive Economic Zone open to all States), Churchill (1996) concludes that this will depend upon whether the activity is a freedom of the high sea and is thus not prohibited under international law, and finds that the other marine treaties will be relevant in this regard.

Finally, the London Convention is considered by Campbell (1996), who focuses particularly on the "industrial waste" definition contained in Annex I list of prohibited substances, but does not provide an opinion upon whether CO_2 is caught by that definition ("waste materials generated by manufacturing or processing operations", or indeed the so-called reverse list exceptions to this prohibition, or to the general prohibition under the 1996 Protocol.

6.8.2 National laws

6.8.2.1 Introduction

CO_2 ocean storage, excluding injection from vessels, platforms or other man-made structures into the sub-seabed to which the assessment made at Section 5.8.1.2 applies, is categorised into the following two types according to the source of injection of the CO_2 (land or sea) and its destination (sea): (1) injection from land (via pipe) into the seawater; (2) injection from vessels, platforms or other man-made structures into seawater (water column, ocean floor).

States are obliged to comply with the provisions of international law mentioned above at Section 6.8.1, in particular treaty law to which they are Parties. States have to implement their international obligations regarding CO_2 ocean storage either by enacting relevant national laws or revising existing ones. There have been a few commentaries and papers on the assessment of the legal position of ocean storage at national level. However, the number of countries covered has been quite limited. Summaries of the assessment of the national legal issues having regard to each type of storage mentioned above to be considered when implementing either experimental or full-fledged ocean storage of CO_2 are provided below.

With regard to the United States, insofar as CO_2 from a fossil-fuel power plant is considered industrial waste, it would be proscribed under the Ocean Dumping Ban Act of 1988. The Marine Protection, Research, and Sanctuaries Act of 1972 (codified as 33 U.S.C. 1401-1445, 16 U.S.C. 1431-1447f, 33 U.S.C. 2801-2805), including the amendments known as the Ocean Dumping Ban Act of 1988, has the aim of to regulating intentional ocean disposal of materials, while authorizing related research. The Ocean Dumping Ban Act of 1988 placed a ban on ocean disposal of sewage sludge and industrial wastes after 31 December 1991.

The US Environmental Protection Agency (US EPA) specified protective criteria for marine waters, which held *p*H to a value between 6.5 and 8.5 with a limit on overall excursion of no more than 0.2 *p*H units outside the naturally occurring range (see: Train, 1979). Much of the early work on marine organisms reflected concerns about the dumping of industrial acid wastes (e.g. acid iron wastes from TiO_2 manufacture) into marine waters. For the most part, however, these studies failed to differentiate between true *p*H effects and the effects due to CO_2 liberated by the introduction of acid into the test systems.

6.8.2.2 Injection from land (via pipe) into seawater

States can regulate the activity of injection within their jurisdiction in accordance with their own national rules and regulations. Such rules and regulations would be provided by, if any, the laws relating to the treatment of high-pressured gases, labour health and safety, control of water pollution, dumping at sea, waste disposal, biological diversity, environmental impact assessment etc. It is, therefore, necessary to check whether planned activities of injection fall under the control of relevant existing rules and regulations.

6.8.2.3 Injection from vessels, platforms or other man-made structures into seawater (water column, ocean floor)

It is necessary to check whether the ocean storage of CO_2 is interpreted as "dumping" of "industrial waste" by relevant national laws, such as those on dumping at sea or waste disposal, because this could determine the applicability of the London Convention and London Protocol. The London Convention and the London Protocol apply to this type of, subject to the issue of whether captured CO_2 constitutes industrial waste or certain exempted material (Section 6.8.1). Even if ocean storage is not prohibited, it is also necessary to check whether planned activities will comply with the existing relevant classes of rules and regulations, if any, mentioned above.

6.9. Costs

6.9.1 Introduction

Studies on the engineering cost of ocean CO_2 storage have been published for cases where CO_2 is transported from a power plant located at the shore by either ship to an offshore injection platform or injection ship (Section 6.9.2), or pipeline running on the sea floor to an injection nozzle (Section 6.9.3). Costs considered in this section include those specific to ocean storage described below and include the costs of handling of CO_2 and transport of CO_2 offshore, but not costs of onshore transport (Chapter 4).

6.9.2 Dispersion from ocean platform or moving ship

Costs have been estimated for ship transport of CO_2 to an injection platform, with CO_2 injection from a vertical pipe into mid- to deep-ocean water, or a ship trailing an injection pipe (Akai *et al.*, 2004; IEA-GHG, 1999; Ozaki, 1997; Akai *et al.*, 1995; Ozaki *et al.*, 1995). In these cases, the tanker ship transports liquid CO_2 at low temperature (-55 to -50ºC) and high pressure (0.6 to 0.7MPa).

Table 6.5 shows storage costs for cases (Akai *et al.*, 2004) of ocean storage using an injection platform. In these cases, CO_2 captured from three power plants is transported by a CO_2 tanker ship to a single floating discharge platform for injection at a depth of 3000m. The cost of ocean storage is the sum of three major components: tank storage of CO_2 onshore awaiting shipping; shipping of CO_2; and the injection platform pipe and nozzle. The sum of these three components is 11.5 to 12.8 \$ per tCO_2 shipped 100 to 500 km. Assuming an emission equal to 3% of shipped CO_2 from boil-off and fuel consumption, the estimated cost is 11.9 to 13.2 \$ per tCO_2 net stored.

Table 6.5. Ocean storage cost estimate for CO_2 transport and injection at 3000 m depth from a floating platform. Scenario assumes three pulverized coal fired power plants with a net generation capacity of 600MWe each transported either 100 or 500 km by a CO_2 tanker ship with capacity 80,000 m^3 to a single floating discharge platform.

Liquid CO_2 could be delivered by a CO_2 transport ship to the injection area and then transferred to a CO_2 injection ship, which would tow a pipe injecting the CO_2 into ocean at a depth of 2,000 to 2,500 m. Estimated cost of ocean storage (Table 6.6) is again the sum of three major components: tank storage of CO_2 onshore awaiting shipping; shipping of CO_2; and the injection ship, pipe and nozzle (Table 6.6; Akai *et al.*, 2004). The sum of these three components is 13.8 to 15.2 \$ per tCO_2 shipped 100 to 500 km. Assuming an emission equal to 3% of shipped CO_2 from boil-off and fuel consumption, the estimated cost is 14.2 to 15.7 \$ per tCO_2 net stored.

Table 6.6. Ocean storage cost estimate for CO_2 transport and injection at 2000-2500 m depth from a moving ship.

6.9.3 Dispersion by pipeline extending from shore into shallow to deep water

Compared with the ship transport option (6.9.2), pipeline transport of CO_2 is estimated to cost less for transport over shorter distances (e.g. 100 km) and more for longer distances (e.g. 500 km), since the cost of ocean storage via pipeline scales with pipeline length.

The cost for transporting CO_2 from a power plant located at the shore through a pipeline running on the sea floor to an injection nozzle has been estimated by IEA-GHG (1994) and Akai *et al.* (2004). In the recent estimate of Akai *et al.* (2004), CO_2 captured from a pulverized coal fired power plants with a net generation capacity of 600MWe is transported either 100 or 500 km by a CO_2 pipeline for injection at a depth of 3000m at a cost of 6.2 $ per tCO_2 net stored (100 km case) to 31.1 $ per tCO_2 net stored (500 km case).

There are no published cost estimates specific to the production of a CO_2 lake on the sea floor; however, it might be reasonable to assume that there is no significant difference between the cost of CO_2 lake production and the cost of water column injection given that dominance of pipeline costs.

6.9.4 Cost of carbonate neutralization approach

Large-scale deployment of carbonate neutralization would require a substantial infrastructure to mine, transport, crush, and dissolve these minerals, as well as substantial pumping of seawater, presenting advantages for coastal power plants near carbonate mineral sources.

There are many tradeoffs to be analyzed in the design of an economically optimal carbonate-neutralization reactor along the lines of that described by Rau and Caldeira (1999). Factors to be considered in reactor design include water flow rate, gas flow rate, particle size, pressure, temperature, hydrodynamic conditions, purity of reactants, gas-water contact area, etc. Consideration these factors has led to preliminary cost estimates for this concept, including capture, transportation, and energy penalties, of 10 to 110 $/tCO_2$ net stored (Rau and Caldeira, 1999).

6.9.5 Cost of monitoring and verification

The cost of a monitoring and verification program could involve deploying and maintaining a large array of sensors in the ocean. Technology exists to conduct such monitoring, but a significant fraction of the instrument development and production is limited to research level activities. No estimate of costs for near-field monitoring for ocean storage have been published, but the costs of limited near-field monitoring would be small compared to the costs of ocean storage in cases of the scale considered in 6.9.2-3. Far field monitoring can leverage off of international research programs that are developing global monitoring networks.

6.10. Gaps

The science and technology of ocean carbon storage could move forward by addressing the following major gaps:

- *Biology and ecology:* Studies of the response of biological systems in the deep sea to added CO_2, including studies that are longer in duration and larger in scale than yet performed.

- *Research facilities:* Research facilities where ocean storage concepts (e.g., release of CO_2 from a fixed-pipe or ship, or carbonate-neutralization approaches) can be applied and their effectiveness

and impacts assessed *in situ* at small-scale on a continuing basis for the purposes of both scientific research and technology development.

- *Engineering:* Investigation and development of technology for working in the deep sea, and the development of pipes, nozzles, diffusers, etc., that can be deployed in the deep sea with flow assurance and be operated and maintained cost-effectively.

- *Monitoring:* Development of techniques and sensors to detect CO_2 plumes and their biological and geochemical consequences.

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Tables

Table 6.1. Amount of additional CO_2 residing in the ocean after atmosphere-ocean equilibration for different atmospheric stabilization concentrations. Uncertainty range represents influence of climate sensitivity to a CO_2 doubling in the range of 1.5 K to 4.5 K (Kheshgi et al., 2005; Kheshgi 2004a). This table considers the possibility of increased carbon storage in the terrestrial biosphere; such an increase, if permanent, would allow a corresponding increase in total cumulative emissions. This table does not consider natural or engineered dissolution of carbonate minerals, which would increase ocean storage of anthropogenic carbon. Amount already in ocean exceeds 500 $GtCO_2$ (= 440 $GtCO_2$ for 1994 (Sabine et al., 2004) plus CO_2 absorption since that time). The long-term amount of CO_2 stored in the deep ocean is independent of whether the CO_2 is initially released to the atmosphere or the deep ocean.

Atmospheric CO_2 stabilisation concentration (ppm)	Total cumulative ocean + atmosphere CO_2 release ($GtCO_2$)	Amount of anthropogenic CO_2 stored in the ocean in equilibrium ($GtCO_2$)
350	*2 880 ± 260*	*2 290 ± 260*
450	*5 890 ± 480*	*4 530 ± 480*
550	*8 350 ± 640*	*6 210 ± 640*
650	*10 460 ± 750*	*7 540 ± 750*
750	*12 330 ± 840*	*8 630 ± 840*
1000	*16 380 ± 1,000*	*10 730 ± 1,000*

Table 6.2. Evaluation of measures described in the text illustrated using schematic model results shown in Figure 6.16. For the Net Present Value measure, the percentage represents the discount rate minus the rate of increase in the cost of CO_2 emission. (If these are equal, the Net Present Value of temporary carbon storage is zero.) Two significant digits shown for illustration exceed the accuracy of model results.

Measure		Atmospheric release	Injection Depth		
			1000 m	2000 m	3000 m
Effective Retained Fraction	at 20 years	0	0.96	1.00	1.00
	at 100 years	0	0.63	0.97	1.00
	at 500 years	0	0.28	0.65	0.85
Airborne Fraction	at 20 years	0.61	0.03	$6. \times 10^{-6}$	$7. \times 10^{-10}$
	at100 years	0.40	0.19	0.02	$9. \times 10^{-4}$
	at 500 years	0.24	0.20	0.12	0.06
Net Present Value (constant emissions cost)	5% per year	0	0.95	1.00	1.00
	1% per year	0	0.72	0.95	0.99
	0.2% per year	0	0.41	0.72	0.85
Global Warming Potential	20 year horizon	1	0.01	$1. \times 10^{-6}$	$6. \times 10^{-10}$
	100 year horizon	1	0.21	0.01	$4. \times 10^{-4}$
	500 year horizon	1	0.56	0.20	0.06

Table 6.3. Relations between ΔpH, changes in pCO_2, and dissolved inorganic carbon concentration calculated for mean deep-sea conditions. Also shown are volumes of water needed to dilute 1 tCO_2 to the specified ΔpH, and the amount of CO_2 that, if uniformly distributed throughout the ocean, would produce this ΔpH.

pH change ΔpH	Increase in CO_2 partial pressure ΔpCO_2 (ppm)	Increase in dissolved inorganic carbon ΔDIC (μmol kg^{-1})	Seawater volume to dilute 1 tCO_2 to ΔpH (m^3)	$GtCO_2$ to produce ΔpH in entire ocean volume
0	0	0	—	—
–0.1	150	30	656,000	2000
–0.2	340	70	340,000	3800
–0.3	580	100	232,000	5600
–0.5	1260	160	141,000	9200
–1	5250	400	54,800	24,000
–2	57,800	3,260	6800	190,000
–3	586,000	31,900	700	1,850,000

Table 6.4. Physiological and ecological processes affected by CO_2 (note that listed effects on phytoplankton are not relevant in the deep sea, but may become operative during large scale mixing of CO_2). Based on reviews by Heisler, 1986, Wheatly and Henry, 1992, Claiborne et al., 2002, Langdon et al., 2003 Shirayama, 2002, Kurihara et al., 2004, Ishimatsu et al., 2004, 2005, Pörtner et al. 2004, 2005, Riebesell, 2004, Feeley et al., 2004 and references therein.

Affected processes	Organisms tested
Calcification	Corals
	Calcareous benthos and plankton
Acid-base regulation	Fish
	Sipunculids
	Crustaceans
Mortality	Scallops
	Fish
	Copepods
	Echinoderms/gastropods
	Sipunculids
N-metabolism	Sipunculids
Protein biosynthesis	Fish
	Sipunculids
	Crustaceans
Ion homeostasis	Fish, crustaceans
	Sipunculids
Growth	Crustaceans
	Scallops
	Mussels
	Fish
	Echinoderms/gastropods
Reproductive performance	Echinoderms
	Fish
	Copepods
Cardio-respiratory functions	Fish
Photosynthesis	Phytoplankton
Growth and calcification	
Ecosystem structure	
Feedback on biogeochemical cycles (elemental stoichiometry C:N:P, DOC exsudation)	

Table 6.5. Ocean storage cost estimate for CO_2 transport and injection at 3000 m depth from a floating platform. Scenario assumes three pulverized coal fired power plants with a net generation capacity of 600MWe each transported either 100 or 500 km by a CO_2 tanker ship with capacity 80,000 m^3 to a single floating discharge platform.

Ship transport distance	100 km	500 km
Onshore CO_2 Storage (US$/t$CO_2$ shipped)	3.3	3.3
Ship transport to injection platform(US$/t$CO_2$ shipped)	2.9	4.2
Injection platform, pipe and nozzle (US$/t$CO_2$ shipped)	5.3	5.3
Ocean storage cost (US$/t$CO_2$ shipped)	11.5	12.8
Ocean storage cost (US$/t$CO_2$ net stored)	11.9	13.2

Table 6.6. Ocean storage cost estimate for CO_2 transport and injection at 2000-2500 m depth from a moving ship.

Ship transport distance	100 km	500 km
Onshore CO_2 Storage (US$/t$CO_2$ shipped)	2.2	2.2
Ship transport to injection ship(US$/t$CO_2$ shipped)	3.9	5.3
Injection ship, pipe and nozzle (US$/t$CO_2$ shipped)	7.7	7.7
Ocean storage cost (US$/t$CO_2$ shipped)	13.8	15.2
Ocean storage cost (US$/t$CO_2$ net stored)	14.2	15.7

Figures

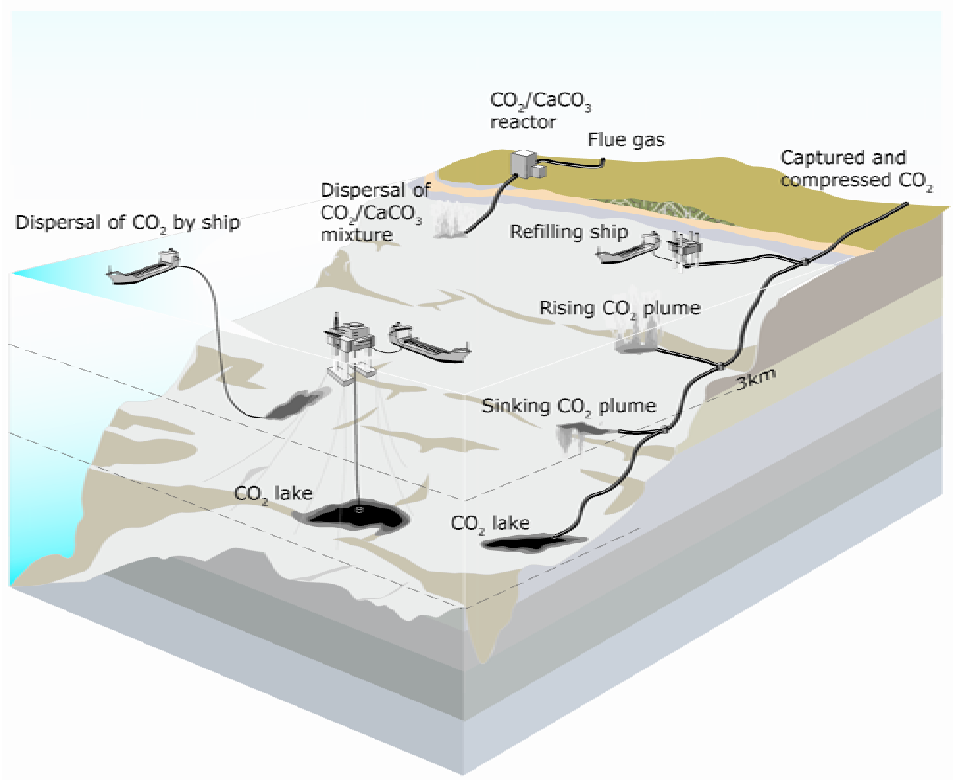

Figure 6.1. Illustration of some of the ocean storage strategies described in this Chapter (figure courtesy Seán Goddard).

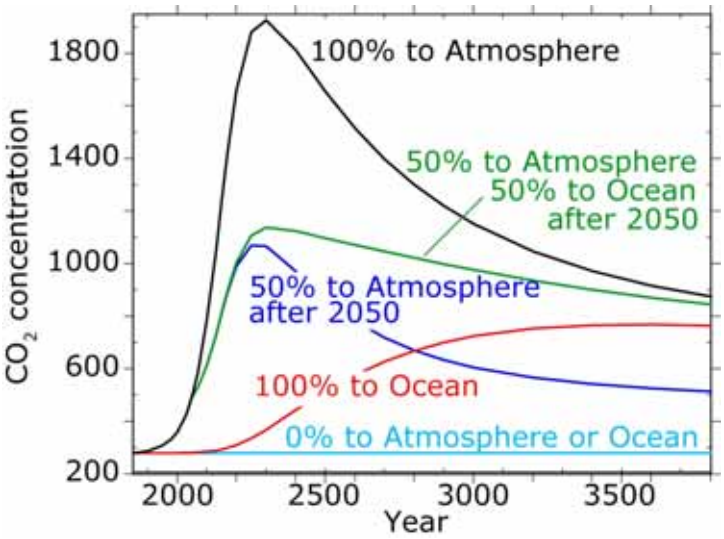

Figure 6.2. Simulated atmospheric CO_2 resulting from CO_2 release to the atmosphere or injection into the ocean at 3,000 m depth (Kheshgi and Archer, 2004). Emissions follow a logistic trajectory with cumulative emissions of 18,000 $GtCO_2$. Illustrative cases include 100% of emissions released to the atmosphere leading to a peak in concentration, 100% of emissions injected into the ocean, and no emissions (e.g. permanent storage). Additional cases include 50% of emissions after 2050 either injected into the ocean (50% to atmosphere and 50% to ocean after 2050) or permanently sequestered (50% to atmosphere after 2050) with emissions prior to 2050 released to the atmosphere. Ocean injection results in lower peak concentrations in these cases. Over millennia, ocean injection cases approach that of atmospheric release. Simulated CO_2 then continues a downward trend due to modelled sediment dissolution.

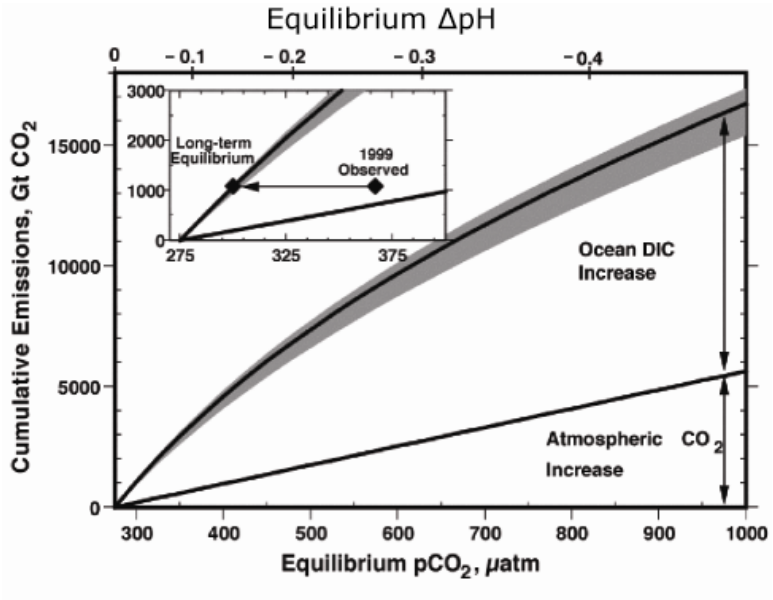

Figure 6.3. Equilibrium partitioning of CO_2 between the ocean and atmosphere. On the time scale of millennia, complete mixing of the oceans leads to a partitioning of cumulative CO_2 emissions between the oceans and atmosphere with the bulk of emissions eventually residing in the oceans as dissolved inorganic carbon. The ocean partition depends non-linearly on CO_2 concentration according to carbonate chemical equilibrium (Box 6.1) and has limited sensitivity to changes in surface water temperature (shown be the grey area for a range of climate sensitivity of 1.5 to 4.5 C for CO_2 doubling) (adapted from Kheshgi et al., 2005; Kheshgi, 2004a). ΔpH evaluated from pCO_2 of 275 ppm. This calculation is relevant on the time scale of several centuries, and does not consider changes in ocean alkalinity that increase ocean CO_2 uptake over several millennia (Archer et al., 1997).

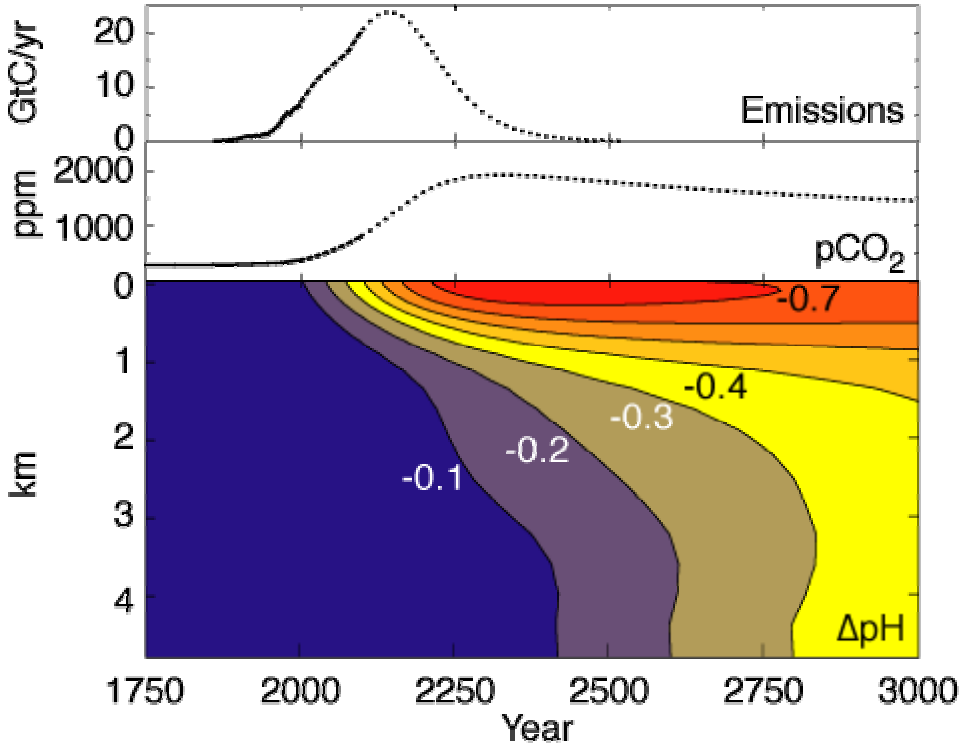

Figure 6.4. Simulated ocean pH changes from CO_2 release to the atmosphere. Modelled atmospheric CO_2 change and horizontally averaged ΔpH driven by a CO_2 emissions scenario: historic atmospheric CO_2 up to 2000, IS92a from 2000 to 2100, and logistic curve extending beyond 2100 with 18,000 $GtCO_2$ (Moomaw et al., 2001) cumulative emissions from 2000 onward (comparable to estimates of fossil fuel resources -- predominantly coal; Caldeira and Wickett, 2003). Since year 1800, the pH of surface of the oceans has decreased about 0.1 pH units (from an initial average surface ocean pH of about 8.2) and CO_3^{2-} has decreased about 40 µmol/kg. There are a number of pH scales used by ocean chemists and biologists to characterize the hydrogen ion content of seawater, but ΔpH computed on different scales varies little from scale to scale (Brewer et al., 1995).

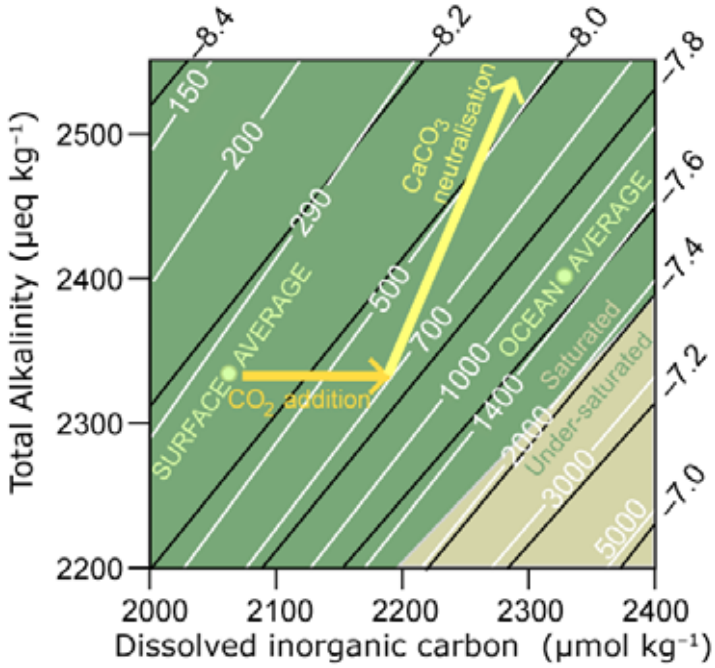

Figure 6.5. Composition diagram for ocean surface waters at 15 °C (adapted from Baes, 1982). The white lines denote compositions with the same value of pCO_2 (in ppm); the black lines denote compositions with the same pH. The tan shaded region is undersaturated and the green shaded region is supersaturated with respect to calcite at atmospheric pressure (calcite solubility increases with depth). Surface water and average ocean compositions are also indicated. Adding CO_2 increases Dissolved Inorganic Carbon (DIC) without changing Total Alkalinity (TAlk); dissolving $CaCO_3$ increases both DIC and TAlk, with 2 moles of TAlk added for each mole of DIC added.

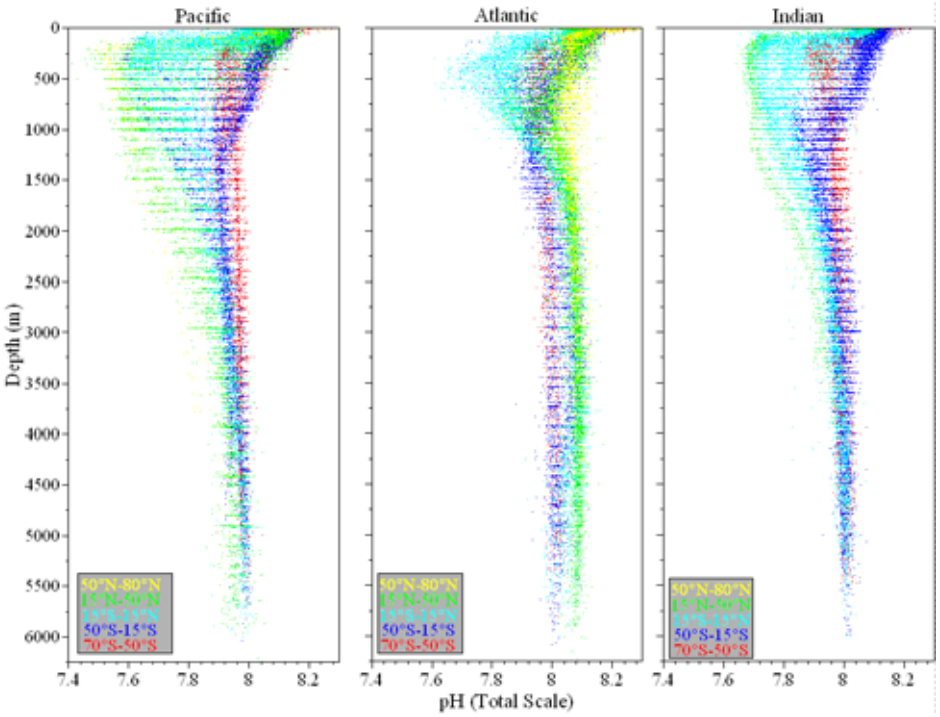

Figure 6.6. Observed variation in open ocean pH for the 1990s (shown on the total hydrogen scale; data from Key et al., 2004). In this figure the oceans are separated into separate panels. The three panels are on the same scale and coloured by latitude band to illustrate the large north-south changes in the pH of intermediate waters. Pre-industrial surface values would have been about 0.1 pH units greater than in the 1990s.

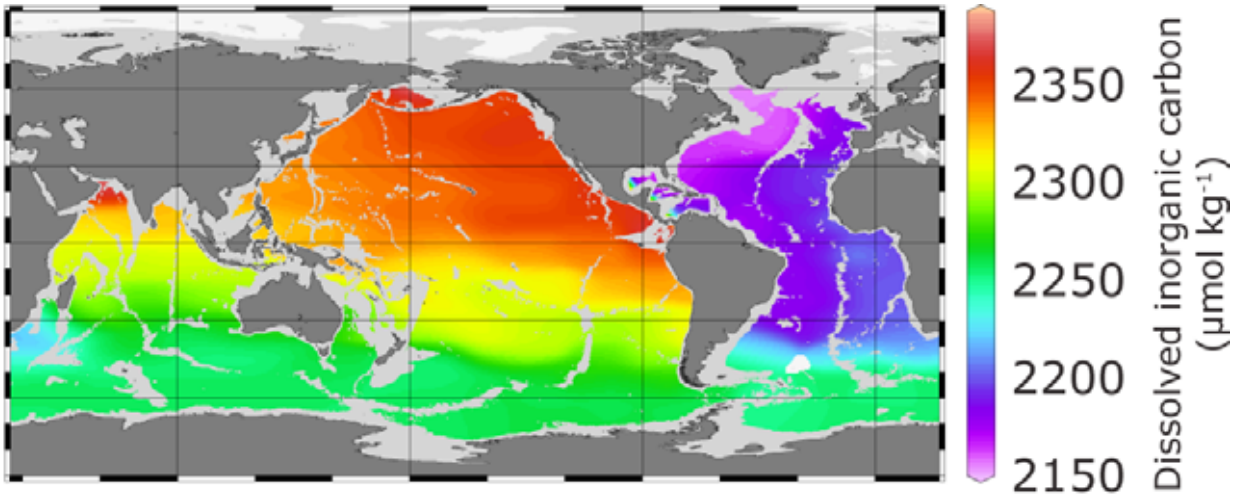

Figure 6.7. Natural variation in dissolved inorganic carbon at 3 km depth. Total dissolved inorganic carbon concentration at 3000 m depth (data from Key et al., 2004). Ocean carbon concentrations increase roughly 10% as deep ocean waters transit from the North Atlantic to the North Pacific due to the oxidation of organic carbon in the deep ocean.

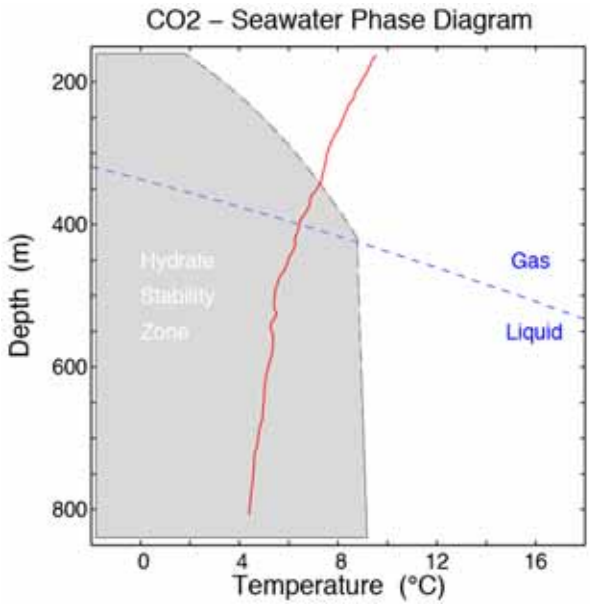

Figure 6.8. CO_2 phases in seawater. CO_2 is stable in the liquid phase when temperature and pressure (increasing with ocean depth) fall in the region below the blue curve; a gas phase is stable under conditions above the blue dashed line. In contact with seawater and at temperature and pressure in the shaded region, CO_2 reacts with seawater to from a solid ice-like hydrate CO_2•6H2O. CO_2 will dissolve in seawater that is not saturated with CO_2. The red line shows how temperature varies with depth at a site off the coast of California; liquid and hydrated CO_2 can exist below about 400 m (Brewer et al., 2004).

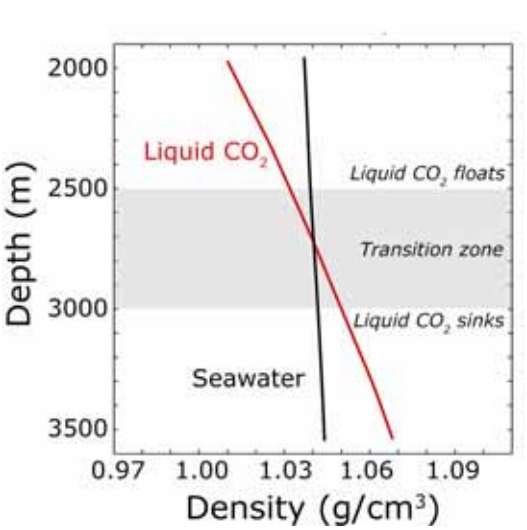

Figure 6.9. Shallower than 2500 m, liquid CO_2 is less dense than seawater, and thus tends to float upward. Deeper than 3000 m, liquid CO_2 is denser than seawater, and thus tends to sink downward. Between these two depths, the behaviour can vary with location (depending mostly on temperature) and CO_2 can be neutrally buoyant (neither rises nor falls). Conditions shown for the Northwest Atlantic Ocean.

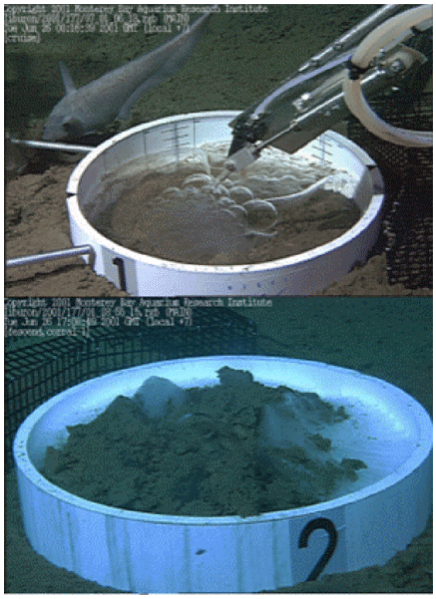

Figure 6.10. Liquid CO_2 released at 3600 meters initially forms a liquid CO_2 pool on the sea floor in a small deep-ocean experiment (b, upper picture). In time, released liquid CO_2 reacts with seawater to form (b, lower picture) a solid CO_2 hydrate in a similar pool.

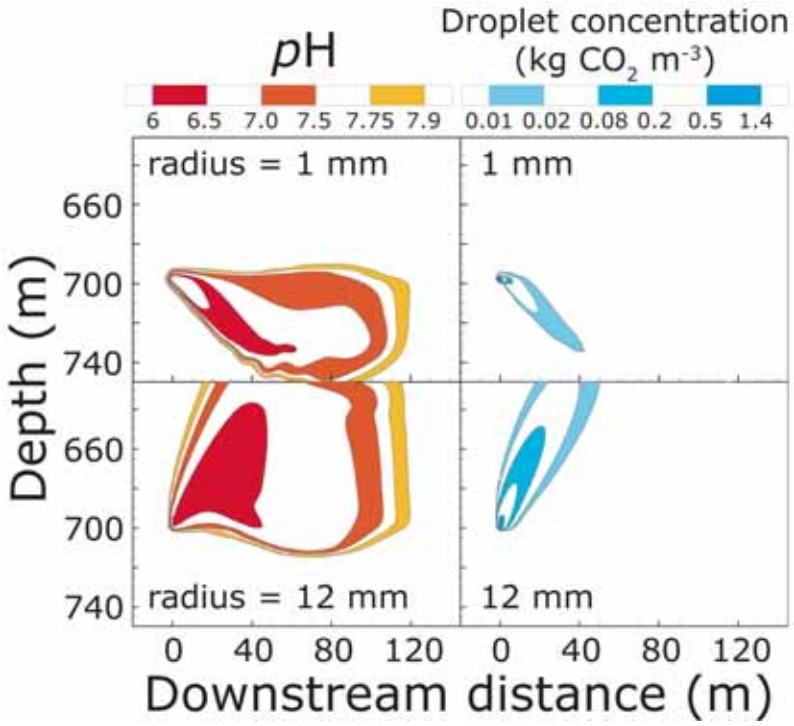

Figure 6.11. Simulated CO_2 enriched seawater plumes (left panels; indicated by pH) and CO_2 droplet plumes (right panels; indicated by kg CO_2/m^3) created by injecting 1-cm and) 12-cm (top and bottom panels, respectively) liquid CO_2 droplets into the ocean from fixed nozzles (elapsed time is 30 min; d injection rate is 1.0 kg CO_2 /sec; ocean current speed is 5 cm/sec; Alendal and Drange, 2001). By varying droplet size, the plume can be made to sink (top panels) or rise (bottom panels).

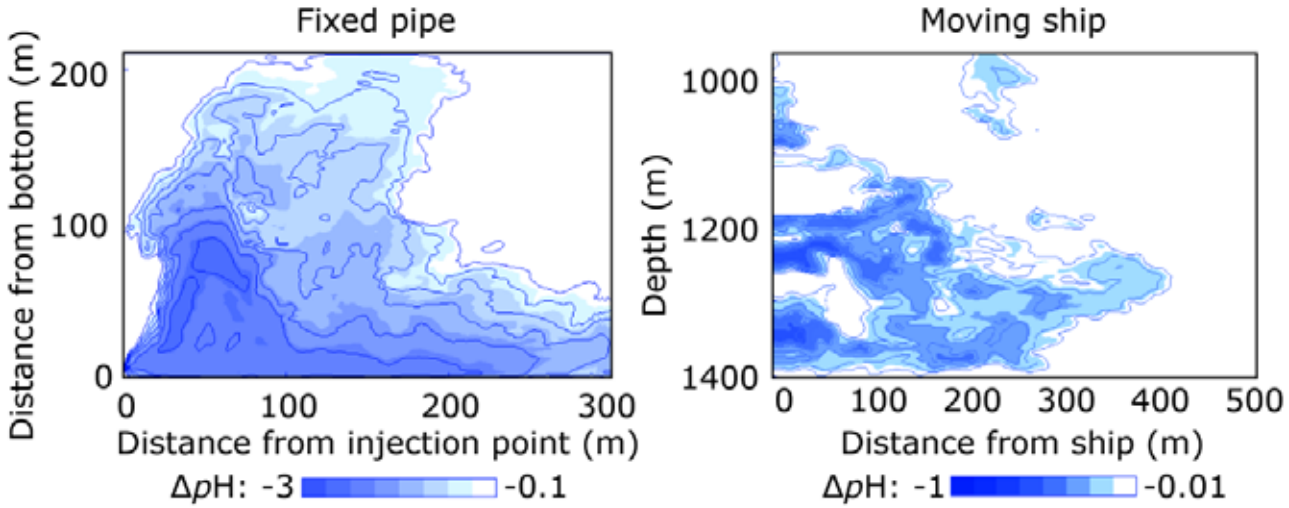

Figure 6.12. Simulated plumes (Chen et al., 2005) created by injecting liquid CO_2 into the ocean from a fixed pipe (left panel) and a moving ship (right panel) at a rate of 100 kg/sec (roughly equal to the CO_2 from a 500 MW_e coal-fired power plant). Left panel: injection at 875 m depth (12m from the sea floor) with an ocean current speed of 2.3 cm/sec. Right panel: injection at 1340 m depth from a ship moving at a speed of 3 m/s. Note difference in pH scales; maximum pH perturbations are smaller in the moving ship simulation.

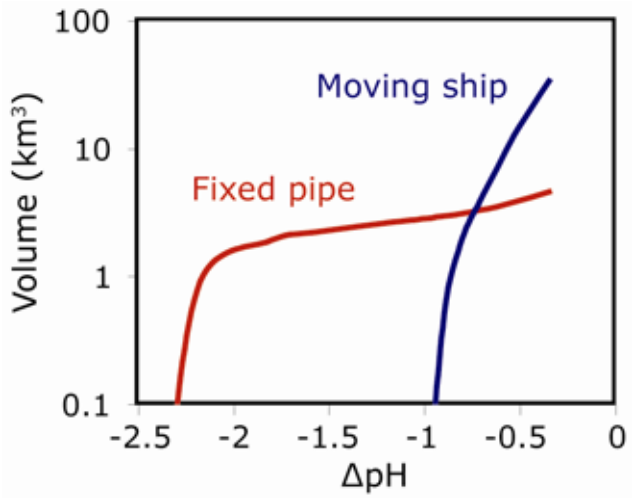

Figure 6.13. Volume of water with a ΔpH less than the value shown on the horizontal axis for the simulations shown in Figure 6.12 corresponding to CO_2 releases from a 500 MW_e power plant. The fixed pipe simulation produces a region with ΔpH < -1; however, the moving ship disperse the CO_2 more widely, largely avoiding pH changes of this magnitude.

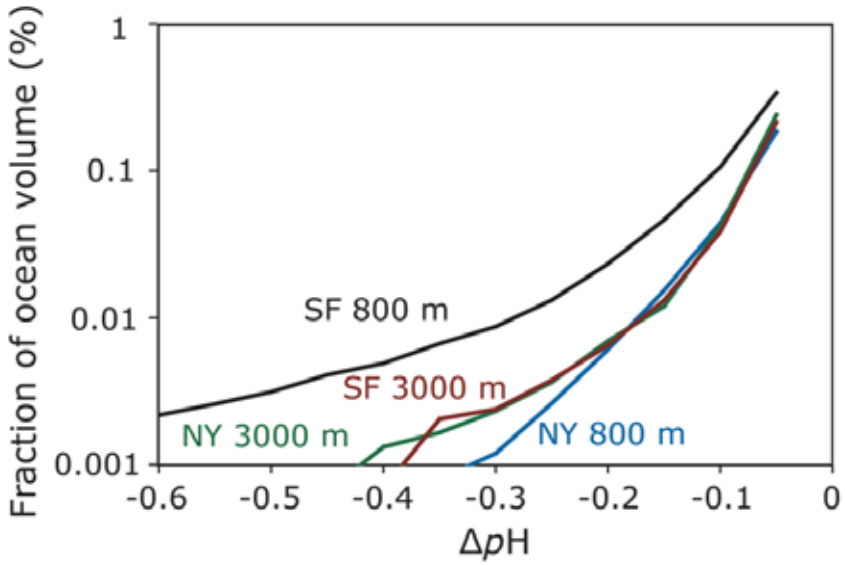

Figure 6.14. Estimated volume of pH perturbations at basin scale (Wickett et al., 2003. Simulated fraction of global ocean volume with a ΔpH less than the amount shown on the horizontal axis, after 100 years of simulated injection at a rate of 0.37 $GtCO_2$ yr^{-1} (= 0.1 GtC yr^{-1}) at each of four different points (two different depths near New York City and San Francisco). Model results indicate, for example, that injecting CO_2 at this rate at a single location for 100 years could be expected to produce a volume of seawater with a ΔpH < -0.3 units in 0.01% or less of total ocean volume (0.01 % of the ocean is roughly 10^5 km^3). As with other simulations of direct CO_2 injection in the ocean, results for the upper ocean (e.g., 800 m) tend to be more site-specific than are results for the deep ocean (e.g., 3000 m).

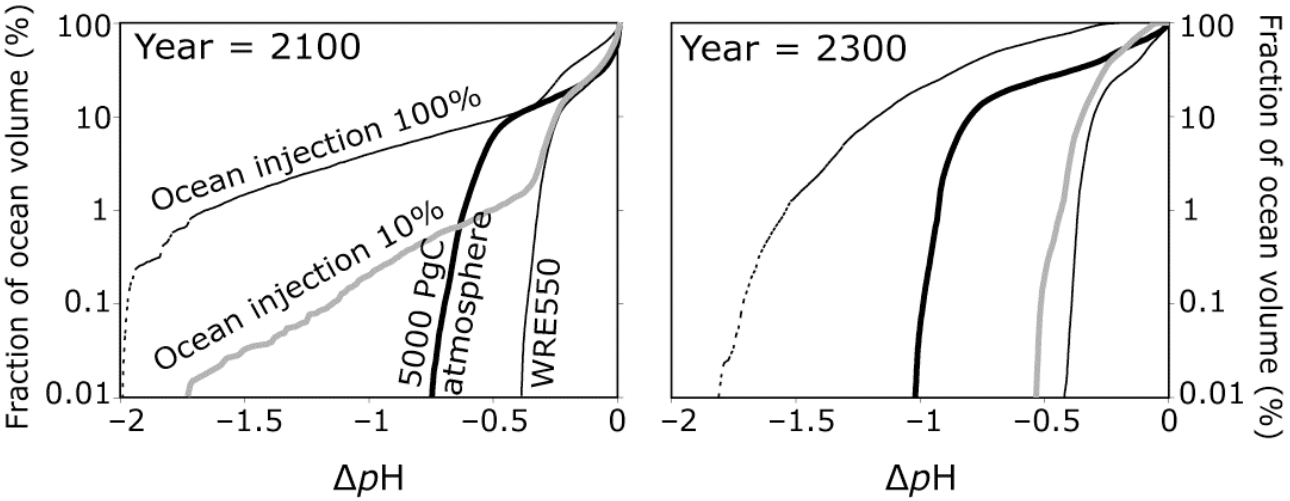

Figure 6.15. Estimated volume of pH perturbations at global scale for hypothetical examples in which injection of CO_2 into the ocean interior provides 100% or 10% of the mitigation effort needed to move from a logistic emissions curve cumulatively releasing 18,000 $GtCO_2$ (=5000 GtC) to emissions consistent with atmospheric CO_2 stabilization at 550 ppm according to the WRE550 pathway (Wigley et al., 1996). Simulated fraction of ocean volume with a pH reduction greater than the amount shown on the horizontal axis. For the 10% case, in year 2100, injection rates are high and on the order of 1% of the ocean volume has significant pH reductions; in year 2300, injection rates are low, but previously injected CO_2 has decreased ocean pH by about 0.1 unit below the value produced by a WRE550 atmospheric CO_2 pathway in the absence of CO_2 release directly to the ocean. (Caldeira and Wickett, 2005).

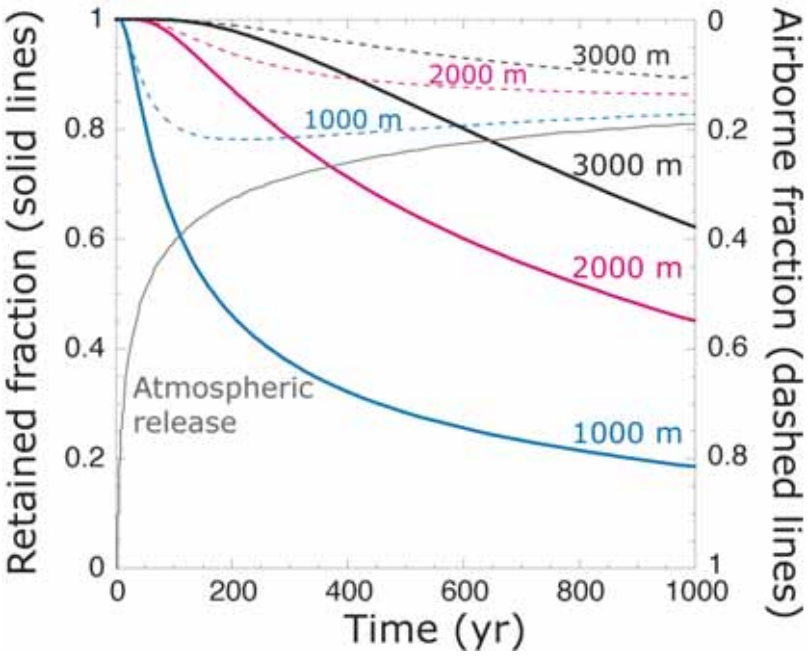

Figure 6.16. Fraction of carbon in the ocean from injection at three different depths and the atmosphere illustrated with results from a schematic model (Herzog et al., 2003). Calculations assume a background 280 ppm of CO_2 in the atmosphere. Solid lines = retained fraction; Dashed lines = airborne fraction. Grey dashed line = airborne fraction for release to atmosphere.

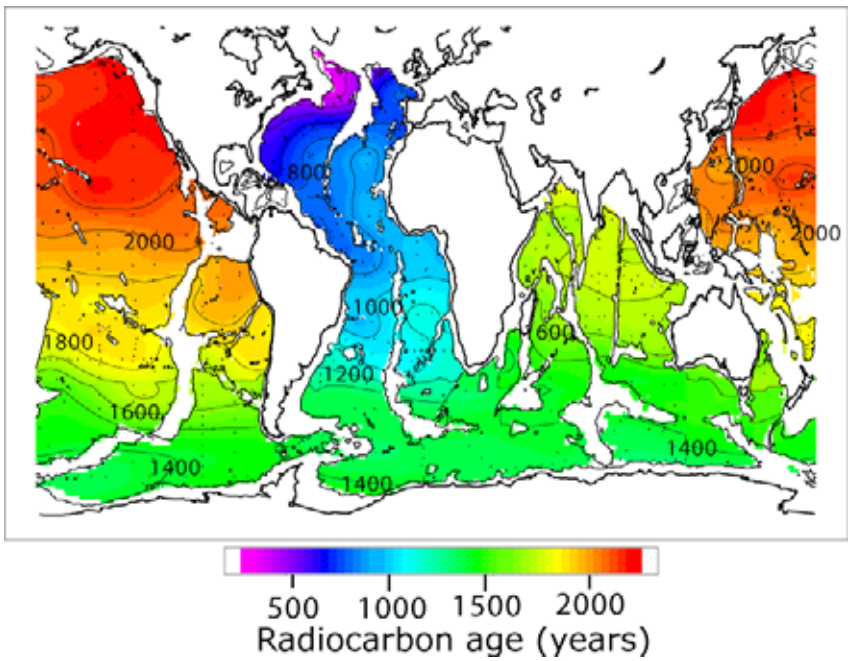

Figure 6.17. Map of radiocarbon (^{14}C) age at 3500 m (Matsumoto and Key, 2004).

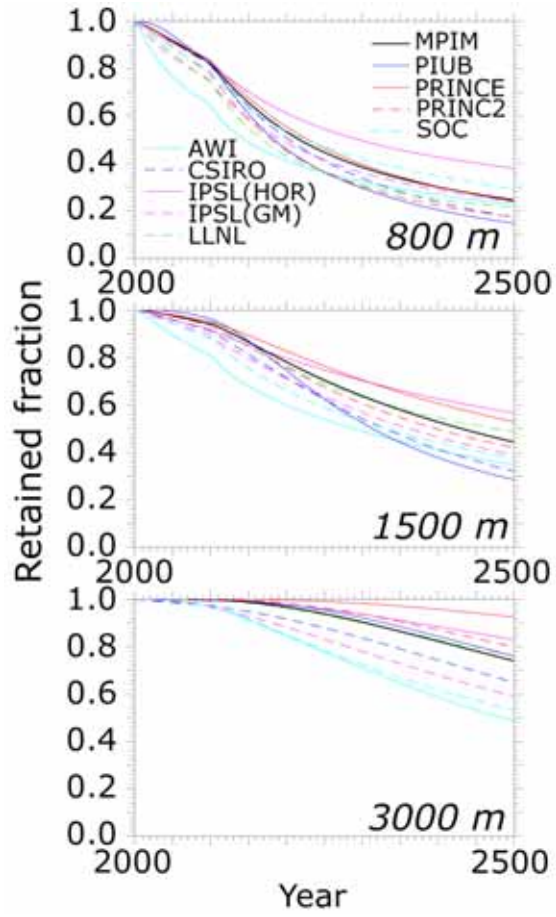

Figure 6.18. Results are shown for seven ocean general circulation models at three different depths averaged over seven injection locations (Orr, 2004). The % efficiency shown is the retained fraction for an injection at a constant rate from 2000 to 2100. Models agree that deeper injection isolates CO_2 from the atmosphere longer than shallower injection. For release at 3000 m, most of the added carbon was still isolated from the atmosphere at the end of the 500 year simulations.

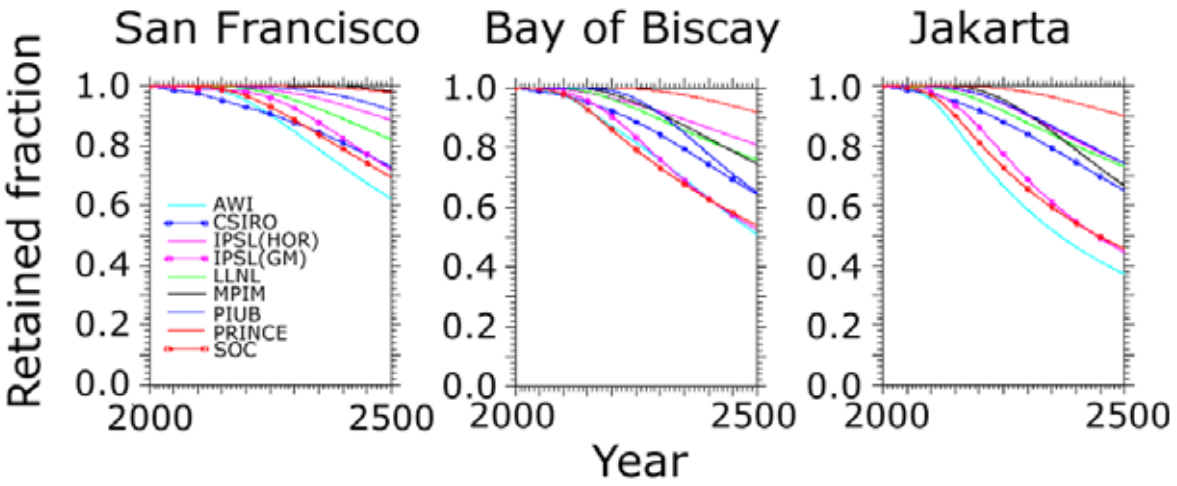

Figure 6.19. Comparison of storage results for three injection locations (at 3000 m depth) in ten ocean model simulations (Orr, 2004). Models differ on predictions of CO_2 retention for release at different locations.

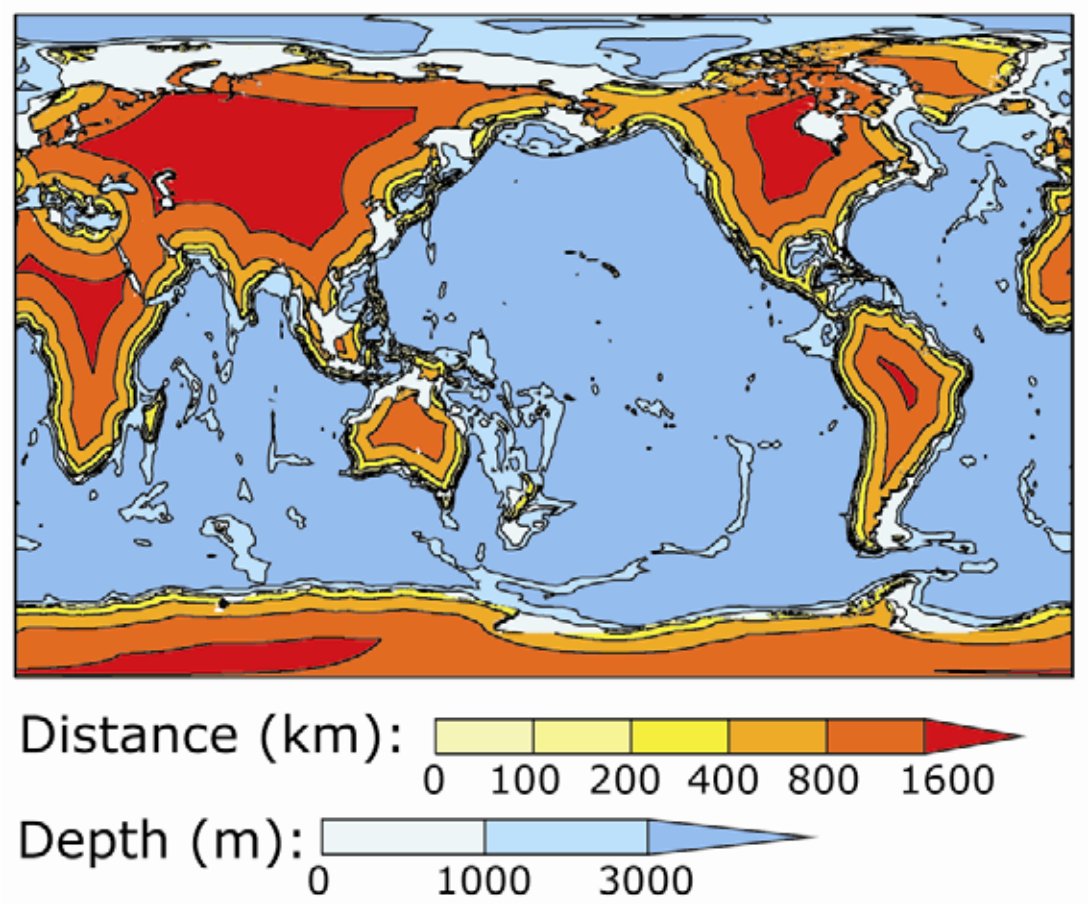

Figure 6.20. For the ocean, location of water at least 1000 m and 3000 m deep; for land, distance to water that is at least 3000 m deep (Caldeira and Wickett, 2005). In general, land areas with the lightest colours would be the most-cost effective land-based settings for a CO_2-injection operation. However, each potential site would need to be evaluated prior to deployment.

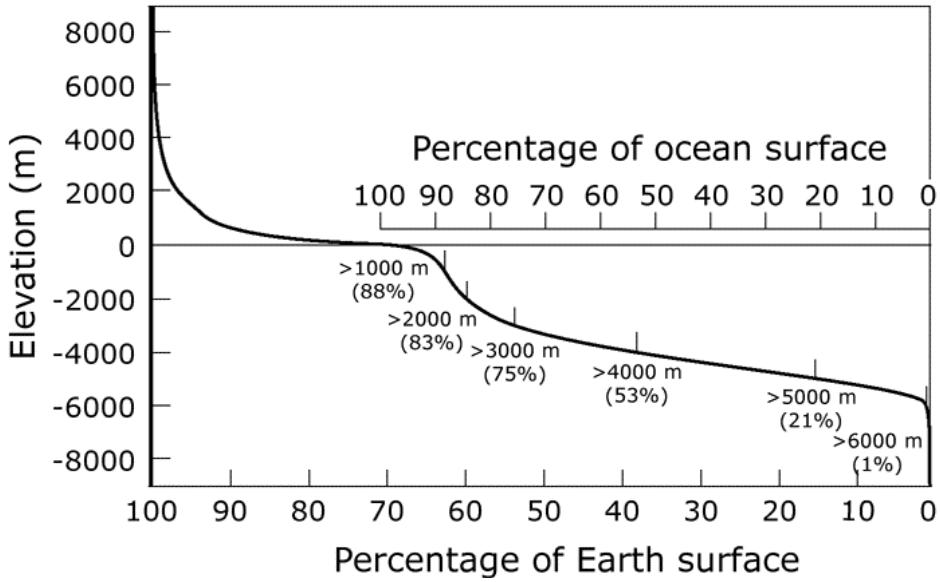

Figure 6.21. Relationship between depth and sea floor area.

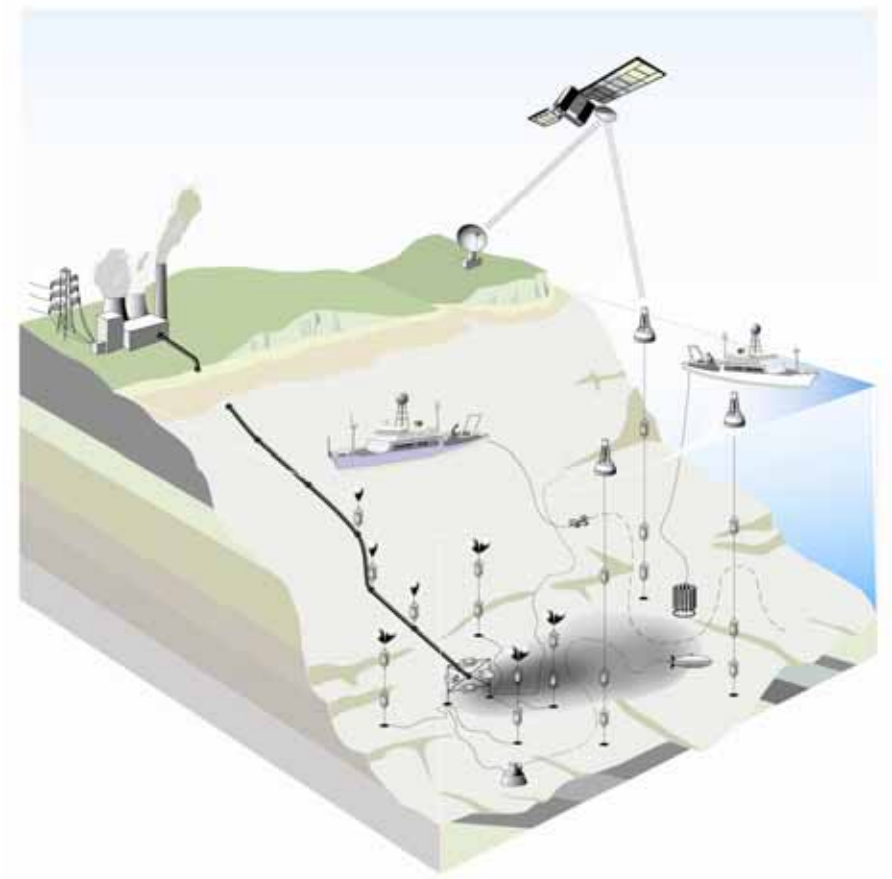

Figure 6.22. Schematic of possible approaches for monitoring the injection of CO_2 into the deep ocean via a pipeline. The grey region represents a plume of high CO_2/low pH water extending from the end of the pipeline. The end of the pipeline is outfitted with two sets of chemical, biological, and current sensors and two underwater cameras to monitor what is emerging from the pipe. An array of moored sensors is located around the pipe to monitor the direction and magnitude of the resulting plume. Carbon sensors are also located along the pipeline to monitor for possible leaks. All of these sensors are wired to a shore based facility to provide power to the sensors and to get real-time data back. An autonomous underwater vehicle maps the near-field distribution of the plume. At distances of more than a few kilometres from the injection site, the plume is monitored with a towed undulating pumping system. The towed system can provide much greater accuracy and precision on the measurements but will also be able to provide measurements over large areas in a relatively short period of time. Moored systems are used to monitor the plume between mapping cruises. These moorings have surface buoys and make daily transmissions back to the monitoring facility via satellite. The very far field distributions are monitored with hydrographic section cruises conducted every 2-5 years using standard discrete sampling approaches. These approaches provide the accuracy and precision required to detect the small CO_2 signals that add to background variations.

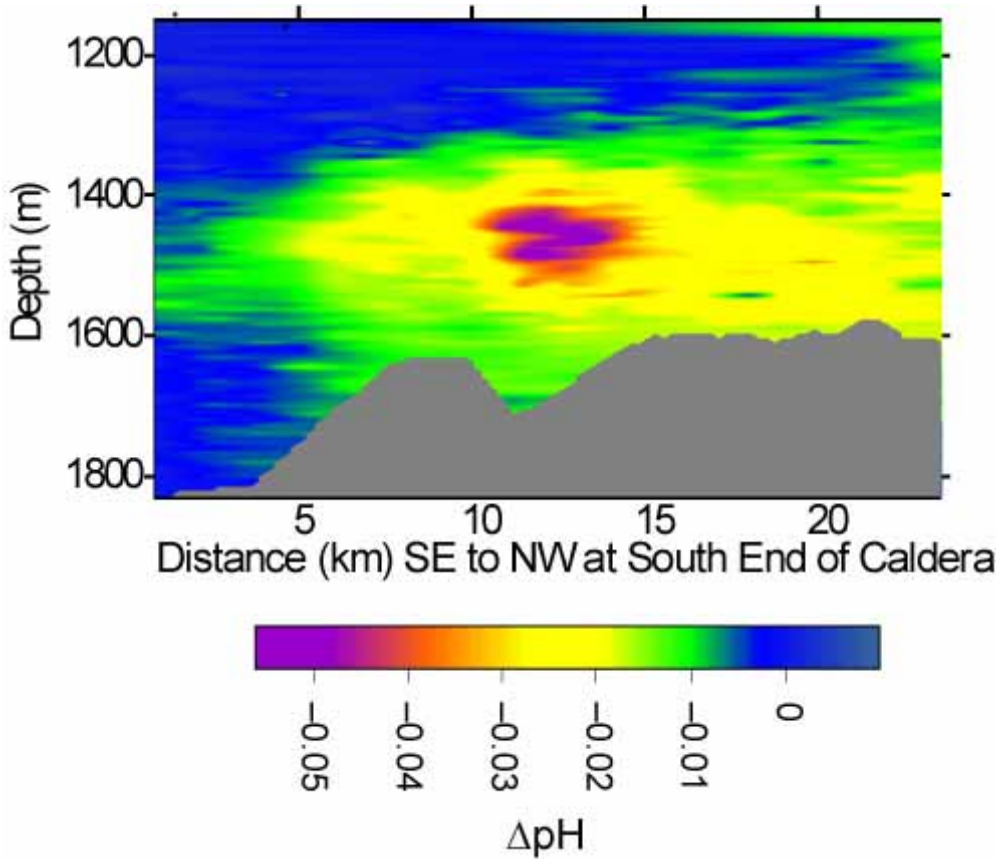

Figure 6.23. Measurements showing the ability to measure chemical effects of a natural CO_2 to plume. Profiles for pH were taken near the Axial Volcano at 46ºN 130ºW, in the ocean near Portland, Oregon, United States, in June 1999.

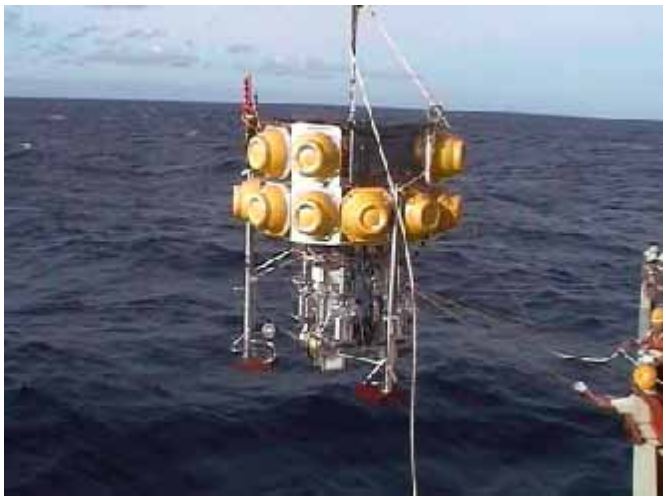

Figure 6.24. Experimental chamber going to the sea floor. The bottom part houses a chamber that penetrates into the sediment. The top part houses electronics, pumps, valves, and water bags, that are used to control the CO_2 concentration inside the chamber, and to sample seawater in the chamber at designated times. At the time of recovery, the bottom of the chamber is closed, weights are released, and the system come back to the surface of the ocean using buoyancy provided by the glass bulbs (yellow structures around the top).

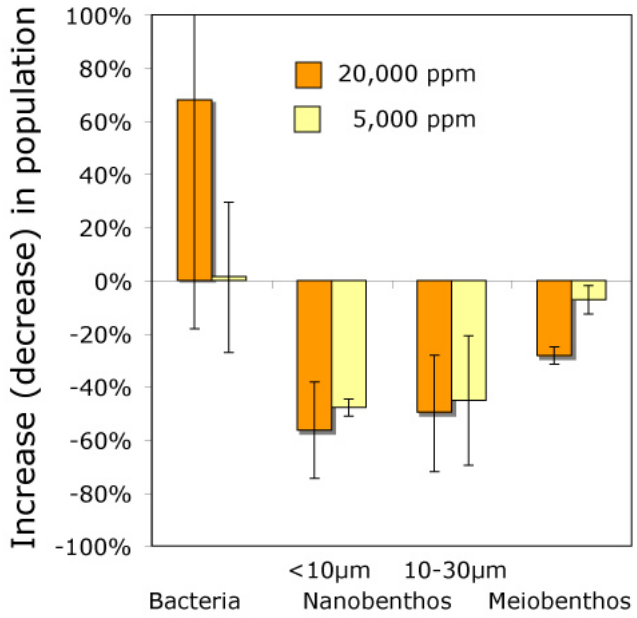

Figure 6.25. Preliminary investigations into the change of bacteria, nanobenthos and meiobenthos abundance after exposure to 20,000 and 5,000 ppm CO_2 for 77 to 375 hr during three experiments carried out at 2,000 m deep in Nankai Trough, North Western Pacific. Error bars represent one standard deviation (Ishida *et al.* 2004).

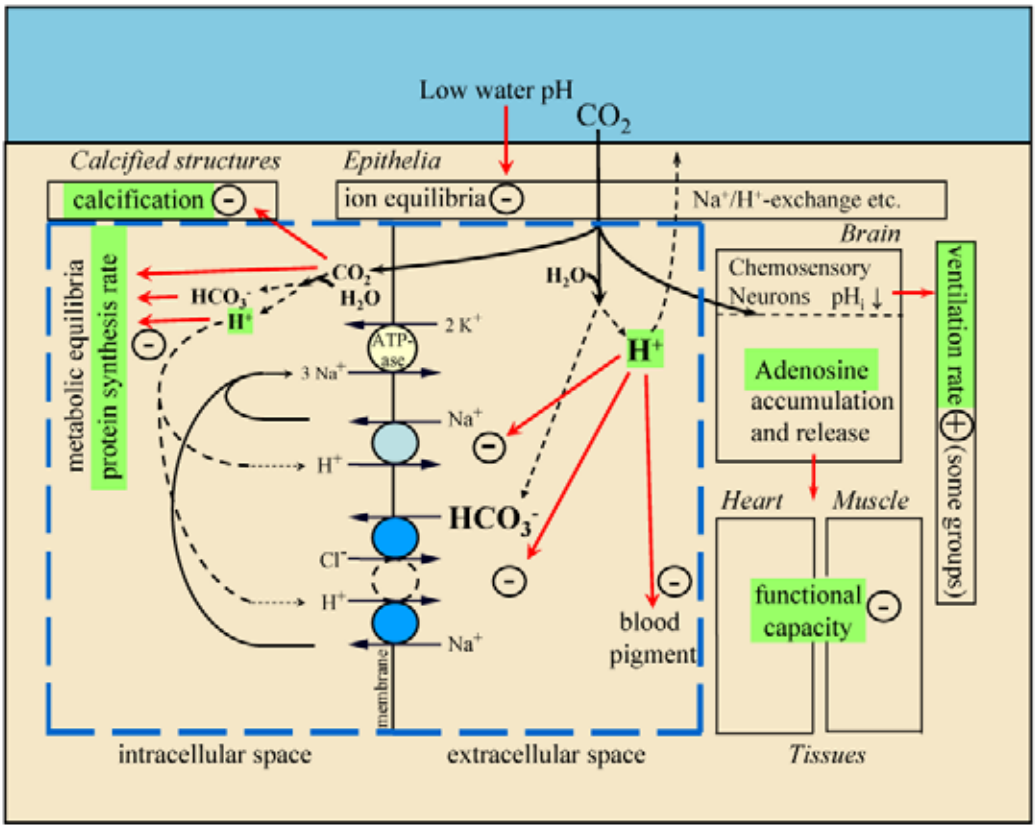

Figure 6.26. Effects of added CO_2 at the scale of molecule to organism and associated changes in proton (H^+), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) levels in a generalized and simplified marine invertebrate or fish. The blue region on top refers to open water; the tan region represents the organism. Generalized cellular processes are depicted on the left and occur in various tissues like brain, heart or muscle; depression of these processes has consequences (depicted on the right and top). Under CO_2 stress, whole animal functions like growth, behaviours, or reproduction are depressed (adopted from Pörtner et al., 2005, - or + denotes a depression or stimulation of the respective function). Black arrows reflect diffusive movement of CO_2 between compartments; red arrows reflect effective factors, CO_2, H^+, HCO_3^- that modulate functions. Shaded areas indicate processes relevant for growth and energy budget.

7. Mineral carbonation and industrial uses of carbon dioxide

Coordinating Lead Author
MARCO MAZZOTTI (ITALY AND SWITZERLAND)

Lead Authors
Juan Carlos Abanades (Spain), Rodney Allam (United Kingdom), Klaus S. Lackner (United States), Francis Meunier (France), Edward Rubin (United States), Juan Carlos Sanchez (Venezuela), Katsunori Yogo (Japan), Ron Zevenhoven (Netherlands and Finland)

Review Editors
Baldur Eliasson (Switzerland), R.T.M. Sutamihardja (Indonesia)

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Executive summary

This Chapter describes two rather different options for CO_2 storage: (i) the fixation of CO_2 in the form of inorganic carbonates, also known as "mineral carbonation or mineral sequestration", and (ii) the industrial utilization of CO_2 as a technical fluid or as feedstock for carbon containing chemicals.

In the case of mineral carbonation (see Section 7.2), captured CO_2 is reacted with metal-oxide bearing materials, thus forming the corresponding carbonates and a solid by-product, e.g. silica. Natural silicate minerals can be used in artificial processes that mimic natural weathering phenomena, but also alkaline industrial wastes can be considered. The products of mineral carbonation are naturally occurring, stable solids that would provide storage capacity on a geological time scale. Moreover, magnesium and calcium silicate deposits are sufficient to fix the CO_2 that could be produced from the combustion of all fossil fuels resources. To fix a tonne of CO_2 requires about 1.6 to 3.7 tonnes of rock. From a thermodynamic viewpoint, inorganic carbonates represent a lower energy state than CO_2; hence the carbonation reaction is exothermic and can theoretically yield energy. However, the kinetics of the natural mineral carbonation are slow; hence all currently implemented processes require energetically intensive preparation of the solid reactants to achieve affordable conversion rates and/or additives that must be regenerated and recycled using external energy sources. The resulting carbonated solids must be stored at an environmentally suitable location. The technology is still in the development stage and is at this point not ready for implementation. The best case studied so far is the wet carbonation of the natural silicate olivine, which involves additional energy requirements of 30 - 50%, and leads to costs between 50 and 100 US$/t$CO_2$ stored.

The industrial use of CO_2 (see Section 7.3) as a gas or a liquid or as feedstock for the production of chemicals could contribute to keeping captured CO_2 out of the atmosphere by storing it in anthropogenic carbon products. Industrial uses provide a carbon sink as long as the pool size keeps growing and the lifetime of the produced compounds is long. Neither pre-requisite is fulfilled in practice, since the scale of CO_2 utilization is small as compared to anthropogenic CO_2 emissions, and the lifetime of the produced chemicals is too short with respect to the scale of interest for CO_2 storage. Therefore, the contribution of industrial uses of captured CO_2 to the mitigation of climate change is expected to be small.

7.1 Introduction

This chapter deals with: (i) the fixation of CO_2 in the form of inorganic carbonates, also known as "mineral carbonation or mineral sequestration" that is discussed in Chapter 7.2, and (ii) the industrial uses of CO_2 as a technical fluid or as feedstock for carbon containing chemicals, which is the subject of Chapter 7.3.

7.2 Mineral Carbonation

7.2.1 Definitions, system boundaries, and motivation

Mineral carbonation is based on the reaction of CO_2 with metal oxide bearing materials to form insoluble carbonates, with calcium and magnesium being the most attractive metals. In nature such a reaction is called silicate weathering and takes place on a geological time scale involving naturally occurring silicates as source of alkaline and alkaline-earth metals, and consuming atmospheric CO_2 at the same time. This chapter deals, however, with so-called mineral carbonation, where high concentration CO_2 from a capture step (see Chapter 3) is brought into contact with

metal oxide bearing materials with the purpose of fixing the CO_2 as carbonates (Seifritz, 1990; Dunsmore, 1992; Lackner *et al.*, 1995). Suitable materials may be abundant silicate rocks, e.g. serpentine and olivine minerals, or on a smaller scale alkaline industrial residues, e.g. slag from steel production or fly ash. In the case of silicate rocks, carbonation can be carried out either *ex-situ* in a chemical process plant after mining and pre-treating the silicates, or *in-situ*, by injecting CO_2 in silicate-rich geological formations or in alkaline aquifers. Industrial residues on the other hand can be carbonated in the same plant where they are produced. It is worth noting that products of *in-situ* mineral carbonation and geological storage may be similar for the fraction of the CO_2 injected for geological storage that reacts with the alkaline or alkaline-earth metals in the cap rock leading to the so-called mineral trapping (see Chapter 5.2.2).

Figure 7.1. Material and energy balances through the system boundaries for a power plant with CO_2 capture and storage through mineral carbonation. The fossil fuel input provides energy both to the power plant that produces CO_2, and to the mineralization process (either directly or indirectly via the power plant). The "other materials" input serves all processes within the system boundaries and includes the metal oxide bearing materials for mineralization. The "other emissions" output is made up of the by-products of the mineralization reaction, i.e. silica and possibly water, as well as of non-reacted input materials.

In terms of material and energy balances, mineral carbonation can be schematized as illustrated in Figure 7.1, which applies to a power plant with CO_2 capture and subsequent storage through mineral carbonation. With respect to the same scheme for a power plant with capture and either geological or ocean storage (see Figure 1.4) two differences can be observed. First, there is an additional material flux corresponding to the metal oxide bearing materials; this is present as input and also as output, in the form of carbonates, silica, non-reacted minerals and for some input minerals product water. Secondly, for the same usable energy output, the relative amounts of fossil fuels as input and of energy rejected as lower grade heat are different. *In-situ* carbonation is an operation similar to geological storage, while on the other hand *ex-situ* carbonation involves processing steps requiring additional energy input that are difficult to compensate for with the energy released by the carbonation reaction. Given the similarities of *in-situ* carbonation with geological storage, this chapter will focus on *ex-situ* mineral carbonation. With present technology there is always a net demand of high grade energy to drive the mineral carbonation process, which is needed for: (i) the preparation of the solid reactants, including mining, transportation, grinding, and activation when necessary; (ii) the processing, including the equivalent energy associated to the use, recycle and possible losses of additives and catalysts; (iii) the disposal of carbonates and by-products. The relative importance of the three items differs depending on the source of the metal oxides, i.e. whether they are natural silicates or industrial wastes.

Figure 7.2. Material fluxes and process steps associated to the *ex-situ* mineral carbonation of silicate rocks or industrial residues (courtesy Energy Research Centre of the Netherlands (ECN)).

Despite this potential energy penalty, interest in mineral carbonation stems from two features that make it unique among the different storage approaches, namely the abundance of metal oxide bearing materials, particularly of natural silicates, and the permanence of storage of CO_2 in a stable solid form. However, mineral carbonation is today still an immature technology. Studies reported in the literature have not yet reached a level where a thorough assessment of the technology potential, costs, and impacts is possible.

7.2.2 Chemistry of mineral carbonation

When CO_2 reacts with metal oxides (indicated here as MO, where M is a divalent metal, e.g. calcium, magnesium, or iron) the corresponding carbonate is formed and heat is released according to the following chemical reaction:

$$MO + CO_2 \rightarrow MCO_3 + \text{heat.} \quad (1)$$

The amount of heat depends on the specific metal and on the material containing the metal oxide. In general this is a large fraction (up to 46% in the case of calcium oxide) of the heat released by the upstream combustion process forming CO_2 (393.8 kJ/molCO_2 for combustion of elemental carbon). In the case of a few natural silicates the following exothermic chemical reactions take place (heat values are given in all cases per unit mole of CO_2 and standard conditions 25°C and 0.1MPa, Robie et al. 1978):

Olivine: $Mg_2SiO_4 + 2\,CO_2 \rightarrow 2\,MgCO_3 + SiO_2$ + 89 kJ/mol CO_2 (2a)
Serpentine: $Mg_3Si_2O_5(OH)_4 + 3\,CO_2 \rightarrow 3\,MgCO_3 + 2\,SiO_2 + 2H_2O$ + 64 kJ/mol CO_2 (2b)
Wollastonite: $CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$ + 90 kJ/mol CO_2 (2c)

Since the reaction releases heat, the formation of carbonates is thermodynamically favoured at low temperature, whereas at high temperature (above 900°C for calcium carbonate, and above 300°C for magnesium carbonate, at a CO_2 partial pressure of 1 bar) the reverse reaction, i.e. calcination, is favoured. The representative member of the olivine family considered in the first reaction above is fosterite, which is iron-free; in nature most olivines contain some iron that can form iron oxides or siderite ($FeCO_3$).

Even at the low partial pressure of atmospheric CO_2 and at ambient temperature, carbonation of metal oxide bearing minerals occurs spontaneously, though on geological time scales (Robie *et al*., 1978; Lasaga and Berner, 1998). Limitations arise from the formation of silica or carbonate layers on the mineral surface during carbonation that tends to hinder further reaction and to limit conversion (Butt *et al*., 1996), and from the rate of CO_2 uptake from the gas phase in the case of aqueous reactions. The challenge for mineral carbonation is to find ways to accelerate carbonation and to exploit the heat of reaction within the environmental constraints, i.e. with minimal energy and material losses.

7.2.3 Sources of metal oxides

Most processes under consideration for mineral carbonation focus on metal oxide bearing material that contain alkaline-earth metals (such as calcium and magnesium) as opposed to alkali metals (such as sodium and potassium) whose corresponding carbonates are very soluble in water. Oxides and hydroxides of calcium and magnesium would be the ideal source materials, but because of their reactivity they are also extremely rare in nature. Therefore, suitable metal oxide bearing minerals may be silicate rocks or alkaline industrial residues, the former being abundant but generally difficult to access, and the latter scarcer but easily available.

Among silicate rocks, mafic and ultramafic rocks are rocks that contain high amounts of magnesium, calcium and iron and have a low content of sodium and potassium; some of their main mineral constituents are olivines, serpentine, enstatite ($MgSiO_3$), talc ($Mg_3Si_4O_{10}(OH)_2$), and wollastonite. Although molar abundances of magnesium and calcium silicates in the earth's crust are similar, rocks containing magnesium silicate exhibit a higher MgO concentration (up to 50 wt%,

corresponding to a theoretical CO_2 storage capacity of 0.55 kg CO_2/kg rock), than rocks containing calcium silicates, e.g. basalts, that have CaO content of about 10 wt% only (with a theoretical CO_2 storage capacity of 0.08 kg CO_2/kg rock) (Goff and Lackner, 1998). Deposits of wollastonite, the most calcium-rich silicate, are much more rare than those of magnesium-rich silicates.

Serpentine and olivine are mainly found in ophiolite belts, i.e., geological zones where colliding continental plates lead to an uplifting of the earth's crust (Coleman 1977). For example, considering ultramafic deposits containing serpentine and olivine in the eastern part of the United States and in Puerto Rico, it was found that they have R_{CO2} values between 1.97 and 2.51, depending on purity and type (the R_{CO2} is the ratio of the mass of mineral needed to the mass of CO_2 fixed when assuming complete conversion of the mineral upon carbonation, i.e. the reciprocal of the theoretical CO_2 storage capacity introduced above). Peridotites and serpentinites exceed the total Mg requirement to neutralize the CO_2 from all worldwide coal resources estimated at 10,000 Gt (Lackner *et al.*, 1995). Specific ore deposits identified in two studies in US and Puerto Rico add to approximately 300 Gt CO_2 (Goff and Lackner, 1998; Goff *et al.*, 2000). This should be compared to CO_2 emissions of about 5.5 $GtCO_2$/yr in the United States and about 24 $GtCO_2$/yr worldwide. No comprehensive mapping of the worldwide storage potential in ophiolite belts has been reported. However, their total surface exposure is estimated to be of the order of 1000 km by 100 km (Goff *et al.*, 2000). It is well known however that magnesium silicate reserves are present in all continents, but since they tend to follow present or ancient continental boundaries, they are not present in all countries. The feasibility of their use for *ex-situ* or *in-situ* mineral carbonation is yet to be established (Brownlow, 1979; Newall *et al.*, 2000).

On a smaller scale, industrial wastes and mining tailings provide sources of alkalinity that are readily available and reactive. Even though their total amounts are too small to substantially reduce CO_2 emissions, they could help introduce the technology. Waste streams of calcium silicate materials that have been considered for mineral carbonation include pulverised fuel ash from coal fired power plants (with a calcium oxide content up to 65 wt%), bottom ash (~20 wt% CaO) and fly ash (~35 wt% CaO) from municipal solid waste incinerators, de-inking ash from paper recycling (~35 wt% CaO), stainless steel slag (~65 wt% CaO and MgO), and waste cement (Johnson, 2000; Fernández Bertos *et al.*, 2004; Iizuka *et al.*, 2004).

7.2.4 Processing

7.2.4.1 Mining and mine reclamation

Mining serpentine would not differ substantially from conventional mining of other minerals with similar properties, e.g. copper ores. Serpentine and olivine are both mined already, although rarely on the scale envisioned here (Goff and Lackner, 1998; Goff *et al.*, 2000). Like in other mining operations, disposal of tailings and mine reclamation are important issues to consider. Tailing disposal depends on their material characteristics, i.e. particle size and cohesion, moisture content, and chemical stability against natural leaching processes, and these depend in turn on the specific process. It is likely that carbonation plants be located near the metal oxide bearing material, either the factory producing the residues to be treated or the silicate mine, so as to avoid transportation of solid materials (see Figure 7.2).

Economies of scale applying to today's mining technology suggests a minimum mining operation of 50,000 to 100,000 tons per day (Hartman, 1992), which translates into a minimum mineable volume of about 0.3 km^3 for a mine with a 30 year lifetime. This is a rather small size for ophiolite ore bodies, which are often kilometres wide and hundreds of meters thick (Goff and Lackner, 1998; Goff *et al.*, 2000; Newall *et al.*, 2000). Since coal, in contrast to ophiolite bodies, occurs in thin

seams and is buried under substantial overburden, it has been argued that a typical above ground coal mine must move more material (Lackner *et al.*, 1995) and disturb a far larger area (Ziock and Lackner, 2000) for the same amount of carbon atoms treated than the equivalent ophiolite mine, assuming maximum conversion of the mineral to carbonate (one carbon atom yields one CO_2 molecule upon combustion, which has to be fixed in one molecule of carbonate).

Serpentine can take many different forms from decorative stones to chrysotile asbestos (O'Hanley, 1996). The possibility of encountering asbestos requires adequate precautions. With current best practice it would reportedly not be an obstacle (Newall *et al.,* 2000). Moreover, since the asbestos form of serpentine is the most reactive, reaction products are expected to be asbestos free (O'Connor et al., 2000). Mineral carbonation could therefore remediate large natural asbestos hazards that occur in certain areas, e.g., in California (Nichols, 2000).

7.2.4.2 Mineral pre-treatment

Mineral pre-treatment outside of the chemical processing steps involves crushing, grinding and milling, as well as some mechanical separation, for example a magnetic extraction of magnetite (Fe_3O_4).

7.2.4.3 CO_2 pre-processing

Mineral carbonation requires little CO_2 pre-processing. If CO_2 is pipelined to the disposal site, the constraints on pipeline operations likely exceed pre-processing needs for mineral carbonation. The current state of research suggests that CO_2 should be used at a pressure similar to the pipeline pressure, thus requiring minimal or no compression (Lackner, 2002; O'Connor *et al*., 2002). Purity demands in carbonation are minimal; acidic components of the flue gas could pass through the same process as they would also be neutralized by the base and could likely be disposed of in a similar manner. Most carbonation processes would preheat CO_2, typically between 100 and 150°C for aqueous processes, whereas in gas-solid reactions temperatures could reach 300 to 500°C (Butt *et al*., 1996).

7.2.4.4 Carbonation reaction engineering

The simplest approach to mineral carbonation would be the reaction of gaseous CO_2 with particulate metal oxide bearing material, at suitable temperature and pressure levels. Unfortunately, such direct gas-solid reactions are too slow to be practical in the case of the materials mentioned in Section 7.2.3 (Newall *et al.*, 2000), and are feasible at reasonable pressures only for refined, rare materials like the oxides or hydroxides of calcium and magnesium (Butt and Lackner, 1997; Bearat *et al.,* 2002; Zevenhoven and Kavaliauskaite, 2004). As a result, mineral carbonation without refined materials cannot directly capture CO_2 from flue gases, but possibly in the case of pressurized CO_2 rich gases from IGCC plants.

Since the direct fixation of carbon dioxide on solid unrefined material particles seems at present not feasible, the alternative requires the extraction of the metal oxide from the solid. This can be accomplished by suspending the solid material in an aqueous solution and by letting it dissolve and release metal ions, e.g. calcium or magnesium ions. These ions come in contact with carbonic acid (H_2CO_3) that is formed in the same solution upon carbon dioxide dissolution. By properly choosing the operating parameters of this single-step or multi-step process, particularly temperature, concentration of possible additives, and CO_2 pressure (that controls the carbonic acid concentration in solution), conditions can be achieved where the carbonate and the by-products, e.g. silica in the case of silicate carbonation, precipitate. At the end of the operation there remains a suspension of fine particles of carbonate, by-products, and non-reacted solid material that have to be separated by

filtration and drying from the solution, whose residual metal ions and additives are to be quantitatively recovered.

This wet process scheme is currently in the research phase and has to overcome three major hurdles to become cost-effective and to be considered as a viable option for carbon storage: (i) acceleration of the overall rate of the process, which may be limited by the dissolution rate of the metal oxide bearing material; (ii) elimination of the interference between the concomitant metal oxide dissolution and carbonate precipitation; (iii) complete recovery of all the chemical species involved, if additives are used.

Mineral carbonation starting from natural silicates is a slow process that can be kinetically enhanced by raising the temperature, which is, however, limited by thermodynamics. In aqueous systems, this is typically kept below 200°C since high temperature favours gaseous CO_2 over precipitated carbonates. It is believed that the metal oxide dissolution constitutes the rate-limiting step, and most research efforts have been devoted to finding ways to speed up the metal oxide extraction from the solid input materials. This could be achieved either by activating the mineral and making it more labile and reactive or by enhancing the metal oxide extraction through the presence of additives or catalysts in solution. Activation can take different forms, namely heat-treatment at 650ºC for serpentine (Barnes *et al.*, 1950; Drägulescu *et al.*, 1972; O'Connor *et al.*, 2000) and ultra-fine (attrition) grinding for olivine and wollastonite (O'Connor *et al*., 2002; Kim and Chung, 2002). The energy cost of activation has been estimated to be of 300 kWh per tonne of mineral, and 70-150 kWh/t of mineral for thermal and mechanical activation, respectively (O'Connor *et al*., 2005). Carbonation has been successfully performed after such pre-treatment, which is however so expensive and energy-intensive to make its feasibility questionable (see Box 7.1 and O'Connor *et al*., 2005). Dissolution catalysts that can be added to the aqueous solution include strong and weak acids (Pundsack, 1967; Lackner *et al.,* 1995; Fouda *et al.,* 1996; Park *et al.,* 2003; Maroto-Valer *et al.*, 2005), bases (Blencoe *et al.,* 2003), and chelating agents to extract SiO_2 or MgO groups from the mineral (Park *et al.,* 2003). All three approaches have been studied and at least partially experimentally tested, but in all cases the catalyst recovery represents the key hurdle. It is worth noting that the carbonation of metal oxides from industrial wastes can be faster than that of natural silicates (Johnson, 2000; Fernández Bertos *et al.*, 2004; Huijgen *et al.*, 2004; Iizuka *et al.*, 2004; Stolaroff *et al.*, 2005).

Hydrochloric acid (HCl) dissolution of serpentine or olivine was proposed first (Houston, 1945; Barnes *et al.*, 1950; Wendt *et al.*, 1998a). The process requires a number of steps to precipitate Mg-hydroxide ($Mg(OH)_2$), which can then directly react with gaseous CO_2, and to recover quantitatively HCl. Exothermic and endothermic steps alternate, and heat recovery is not always possible, thus making the overall process very energy-intensive and not viable (Wendt *et al.*, 1998a; Lackner, 2002; Newall *et al.*, 2000). Likewise, strong alkaline solutions (with NaOH) will dissolve the silica from the magnesium silicate, thus allowing for further digestion of the remaining ($Mg(OH)_2$); however, also in this case the recovery of the NaOH catalyst seems to be very difficult (Blencoe *et al.,* 2003). To overcome the substantial energy penalty of water evaporation in the hydrochloric acid process, it was proposed to dissolve the silicate minerals in a magnesium-chloride melt in order either to precipitate $Mg(OH)_2$ as before or to allow for direct carbonation in the melt (Wendt *et al.*, 1998a; 1998b; 1998c; 1998d). No experimental demonstration of this process has been provided, possibly also because of the corrosive conditions of the reaction; energy and material balances indicate that either version of the process will hardly be viable (Haywood *et al.*, 2001; Newall *et al.*, 2000).

Weaker acids that might reduce the energy requirements for recovery include acetic acid (Kakizawa *et al.*, 2001), oxalic acid (Park *et al.*, 2003), orthophosphoric acid (Park *et al.*, 2003), and ammonium bisulfate (Pundsack 1967). Among the possible chelating agents, that keep either silicates or magnesium ions in solution by forming water-soluble complexes, is EDTA, i.e. ethylene-diamine-tetra-acetic acid (Carey *et al.*, 2003; Park *et al.*, 2003; Park and Fan, 2004). Citric acid is also effective because it combines its acid properties with strong chelating properties (Carey *et al.*, 2003). All these additives have proven to enhance the dissolution of silicate minerals, but only in the acetic acid case a complete process scheme including acid recovery has been described and evaluated (Kakizawa *et al.*, 2001). This is based on two steps, whereby the metal ions are extracted first using acetic acid, and then the carbonate is precipitated upon CO_2 addition; acetic acid remains always in solution as either calcium or magnesium acetate or free acid and can be recycled. The process has been demonstrated for wollastonite only. Experimental conversion levels of the wollastonite have not exceeded 20% (Kakizawa *et al.*, 2001).

7.2.4.5 A worked out example: single step carbonation

Figure 7.3 illustrates the single step wet mineral carbonation process that can be applied to natural silicates as well as to industrial residues, e.g. steel slag (Huijgen *et al*., 2004). The figure refers to the carbonation of olivine, whereby the mineral is ground first. Subsequently, it is dissolved in an aqueous solution of sodium chloride (NaCl, 1 mol/L) and sodium bicarbonate ($NaHCO_3$, 0.64 mol/L) in contact with high pressure CO_2 and carbonated therein (O'Connor *et al*., 2002; O'Connor *et al*., 2005). The additives are easily recovered upon filtration of the solid particles, since the sodium and chloride ions do not participate in the reaction and remain in solution, whereas the bicarbonate ion is replenished by contacting the solution in the carbonation reactor with the CO_2 atmosphere. A maximum conversion of 81% in 1 hour was obtained with an olivine of 37 micron particle size, at a temperature of 185°C and a CO_2 partial pressure of 15 MPa. An important element of the process scheme in Figure 7.3 is the classification (sieving) that allows separating the carbonate and silica products from the olivine that has to be recycled. This is possible since non-reacted olivine minerals are coarse, whereas the carbonate and silica consist of finer particles (O'Connor *et al*., 2002). An additional difficulty of single step carbonation is when upon extraction of the metal oxide from the solid particles a silica layer forms or a carbonate layer precipitates on the particles themselves, thus hindering further dissolution. Experimental evidence indicates that this does not occur in the case of olivine (O'Connor *et al*., 2002), whereas it occurs in the case of steel slag (Huijgen *et al*., 2004).

Figure 7.3. Process scheme of the single step mineral carbonation of olivine in aqueous solution (courtesy Albany Research Centre). "Single step" indicates that mineral dissolution and carbonate precipitation take place simultaneously in the same carbonation reactor, whereas more steps are of course needed for the whole process including preparation of the reactants and separation of the products.

With the process scheme of Figure 7.3 at hand, it is possible to calculate the material balances by considering that the molecular mass of carbon dioxide is 44.0 g/mol, of magnesium carbonate is 84.3 g/mol, of silica is 60.1 g/mol, and of olivine is 140.7 g/mol. For the sake of simplicity only two assumptions are made, namely the degree of conversion in the carbonation reactor, i.e. the fraction of olivine fed to the reactor that is converted to carbonate in a single pass, and the fraction of non-reacted mineral in the classifier that is not recycled but ends up with the material to be disposed of. Based on the stoichiometry of the carbonation reaction 1.6 tons of olivine would be needed to fix one ton of CO_2, thus producing 2.6 tonnes of solid material for disposal. Assuming 90% carbonation conversion and 10% losses in the classifier, one would need 1.62 tonnes of olivine and

should dispose of 2.62 tonnes of solids per tonne of CO_2 mineralized. Assuming 50% conversion only and as many as 20% losses, for one tonne of CO_2 stored 1.87 tonnes of olivine would be needed and 2.87 tonnes would be disposed of. In the latter case, however the carbonation reactor would be twice as big as in the former case.

Olivine has the highest concentration of reactive magnesium oxide among the natural minerals (57% by weight). Other minerals in general contain a lower concentration; for pure serpentine the magnesium oxide concentration is about 44%; for typical ores the concentration can be 50% of that of the pure mineral. Therefore, the mineral feedstock required to fix 1 tonne of CO_2 in carbonates is between 1.6 and 3.7 tonnes, and the process yields between 2.6 and 4.7 tonnes of products to be handled. The carbonation process consumes energy and thus causes CO_2 emissions that reduce accordingly the net storage of CO_2. For the olivine carbonation process having the lowest unit cost among those described in Box 7.1, the energy requirement is 1.1 GJ/tCO_2; if this is provided by the same coal derived electricity it would cause CO_2 emissions equal to 30% of the fixed CO_2.

7.2.5 Product handling and disposal

Disposal options for mineral carbonates are determined by the mass of the resulting material (see Figure 7.2). It is not cost-effective to ship the bulk of these materials over long distances. As a result the obvious disposal is at the mine site itself. Like in any large-scale mining operations, the logistics of mining out a site and reclaiming it after refilling it with the tailings is substantial, but it does not pose novel problems (Newall *et al.,* 2000). The amount of material to be disposed of is between 50 and 100% by volume more than that originally mined. This volumes are comparable to volumes commonly handled in mining operations and are subject to standard practice of mine reclamation (Lackner *et al.*, 1997; Newall *et al.,* 2000).

The fine grinding of the mineral ore might allow for the extraction of mineral constituents of value. Serpentine and olivine mines could provide iron ore that either would be removed as magnetite in a magnetic separation or result from a chemical precipitation during magnesium extraction yielding concentrated iron oxide or hydroxide (Park and Fan, 2004). Peridotite rocks may contain chromite, elements like nickel and manganese, and also elements in the platinum group, but how to recover these has still to be studied (Goff and Lackner, 1998). It has been suggested, that magnesium carbonate and silica may find uses as soil enhancer, roadfill or filler in a mining operation. Eventually mineral carbonation would have to operate at scales that would saturate any product or by-product market, but products and by-products when usable could help make a demonstration of the process more viable (Lackner *et al.,* 1997; Goff and Lackner, 1998).

7.2.6 Environmental impact

The central environmental issue of mineral carbonation is the associated large-scale mining, ore preparation and waste-product disposal (Goff and Lackner, 1998). It can directly lead to land-clearing and the potential pollution of soil, water and air in surrounding areas. It may also indirectly result in habitat degradation. An environmental impact assessment would be required to identify and prevent or minimize air emissions, solid waste disposal, wastewater discharges, water use, as well as social disturbances. As for many other mining activities, the preventing and mitigating practices are relatively basic and well developed.

Land-clearing: The amount of material required to store CO_2 involves extensive land clearing and the subsequent displacement of millions of tonnes of earth, rock and soil, increasing the potential for erosion, sedimentation and habitat loss in the area. Access roads would also lead to clearing of vegetation and soil. Standard practices recommended to minimize these impacts include storage of topsoil removed for use in future reclamation activities, use of existing tracks in constructing access roads and pipelines, and use of drainage and sediment collection systems to catch runoff or divert surface water, minimizing erosion.

Air quality: Mining activities like blasting, drilling, earth-moving and grading can generate dust and fine particulate matter that affect visibility and respiration, and pollute local streams and vegetation. Dust prevention measures are widely applied at mining operations today, but if not properly controlled dust can threaten human respiratory health. This is particularly important in serpentine mining because serpentine often contains chrysotile, a natural form of asbestos. Even though chrysotile is not as hazardous as amphibole asbestos (tremolite, actinolite) (Hume and Rimstidt, 1992), the presence of chrysotile requires covering of exposed veins and monitoring of air quality (Nichols, 2000). On the other hand, mineral carbonation products are asbestos free, as the reaction destroys chrysotile, that reacts faster than other serpentines, even if conversion of the starting material is not complete, thus possibly making mineral carbonation an effective method for the remediation of asbestos in serpentine tailing (O'Connor et al., 2000). The resulting mineral carbonates are inert, but large volumes of powders would also have to be controlled for example by cementing them together to avoid contamination of soil and vegetation, as well as habitat destruction.

Tailings: Tailings consist of finely ground particles, including ground-up ore and process by-products. Tailings management systems should be designed and implemented from the earliest stages of the project. Usually tailings are stored in tailings impoundments designed to hold tailings behind earth-fill dams (Newall *et al.*, 2000). Other control measures depend on whether tailings are dry or wet, on particle size and chemical reactivity.

Leaching of metals: Although the low acidity of the resulting by-products reduces the possibility of leaching, certainty about leaching can only be obtained by conducting tests. If necessary a liner system would prevent groundwater contamination. Leaching containment is also possible without lining where underlying rock has shown to be effectively impermeable.

Reclamation: A comprehensive reclamation program has to be designed during the planning phase of the mining project, and be implemented concurrently throughout operations to minimize water contamination, restore wildlife habitat and ecosystem health and improve aesthetic of the landscape. Concurrently incorporation of reclamation with the mining of the site reduces waste early, prevents clean-up costs and decreases potential liabilities. Land rehabilitation will involve the re-shaping of landform, because the volume of tailings will be larger than the mined rock. The main environmental concern regarding reclamation includes major soil movements by erosion or landslides. This can be controlled by an adequate vegetation cover and by covering the soil with protective mulch, by maintaining moisture in the soil, or by constructing windbreaks to protect the landform from exposure to high winds.

7.2.7 Life Cycle Assessment and Costs

At the development stage of today, mineral carbonation consumes additional energy and produces additional CO_2 as compared to other storage options, as shown in Figure 7.1, and that is why a Life Cycle Assessment of the specific process routes is particularly important. The potential of mineral

carbonation depends on the trade-off between costs, associated to the energy consuming steps (mining, pre-processing of the mineral ore, and subsequent disposal and mine reclamation), and benefits (the large potential capacity due to the vast availability of natural metal oxide bearing silicates and the permanence of CO_2 storage).

A life-cycle analysis of the mining, size reduction process, waste disposal and site restoration lead to additional annual CO_2 emissions of 0.05 tCO_2 per tonne of CO_2 stored (Newall *et al*., 2000). This included grinding of the rock to particles size less than 100 micron; a ratio of 2.6 tonnes of serpentine per tonne of CO_2 was assumed. The cost was assessed to be about 14 US$/$tCO_2$ stored, the capital cost being about 20% of the total. All costs estimates were based on OECD Western labour costs and regulations; the conversion factor from electrical energy to CO_2 emissions was 0.83 tCO_2/MWh electricity; costs were calculated on the basis of an electricity price of 5 ct/kWh electricity; results from other studies were converted using these values (Newall *et al*., 2000). Other estimates of these costs are between 6 and 10 US$/$tCO_2$ stored, with 2% additional emissions (Lackner *et al.*, 1997).

As far as the scale of mining and disposal is concerned, i.e. about 1.6 to 3.7 tonnes of silicate and 2.6 to 4.7 tonnes of disposable materials per ton of CO_2 fixed in carbonates as reported in Section 7.2.4, this is of course a major operation. When considering that one tonne of carbon dioxide corresponds to 0.27 tonnes of carbon only in theory, but in practice to about 2 tonnes of raw mineral due to the overburden, it follows that mineral carbonation to store the CO_2 produced by burning coal would require the installation of a mining industry of a comparable scale as the coal industry itself. Such large mining operations are significant, but placing them in context of the operations needed for the use of fossil fuels, and geological or ocean storage, the volumes are comparable.

The energy requirements and the costs of the carbonation reaction are very much process dependent and more difficult to estimate, due to scarcity of data. The most detailed study has been carried out for the process where the silicates are dissolved in a magnesium chloride melt (Newall *et al*., 2000). An overall cost (including the operations mentioned in the previous paragraph) of 80 US$/$tCO_2$ stored was obtained, with 27.5% additional CO_2 emissions, thus leading to 110 US$/$tCO_2$ avoided. In the case of the two-step acetic acid process, an overall cost of 27 $/t CO_2 avoided has been reported, but the assumptions are based on a rather limited set of experimental data (Kakizawa *et al.*, 2001). A comprehensive energy and economic evaluation of the single step wet carbonation process illustrated in Figure 7.3 has been recently reported (O'Connor *et al*., 2005), and is discussed in detail in Box 7.1. This study calculates that the most favourable implementation leads to a storage cost of 80 US$/$tCO_2$ avoided. No similar economic evaluation is available for either dry mineral carbonation or carbonation using industrial residues. However, it is worth pointing out that the carbonation of toxic wastes may lead to stabilized materials with reduced leaching of heavy metals. Therefore these materials might be disposed of more easily or even used for applications, e.g. in construction work (see Figure 7.2) (Venhuis and Reardon, 2001; Meima *et al*., 2002).

Once the carbon has been stored through mineral carbonation, there are virtually no emissions of CO_2 due to leakage. To the extent that weathering at the disposal site occurs and leaches out magnesium carbonate from the carbonation products, additional CO_2 would be bound in the transformation of solid magnesium carbonate to dissolved magnesium bicarbonate (Lackner, 2002). It can be therefore concluded that the fraction of carbon dioxide stored through mineral carbonation that is retained after 1000 years is virtually certain to be 100%. As a consequence, the needs for monitoring the disposal sites in the case of mineral carbonation are limited.

7.2.8 Future scope

7.2.8.1 Public acceptance

Public acceptance of mineral carbonation is contingent on the broader acceptance of CCS. Acceptance might be enhanced by the fact that this method of storage is highly verifiable and unquestionably permanent. On the downside, mineral carbonation involves large-scale mining and associated environmental concerns: terrain changes, dust pollution exacerbated by the potential for asbestos contamination, and potential trace element mobilization. Generally, public acceptance will require a demonstration that everything possible is done to minimize secondary impacts on the environment.

7.2.8.2 Gap analysis

Mineral carbonation technology must reduce costs and reduce the energy requirements associated with mineral pre-treatment, by exploiting the exothermicity of the reaction. Mineral carbonation will always be more expensive than most applications of geological storage, but in contrast has a virtually unlimited permanence and minimal monitoring requirements. Research towards reducing costs for the application of mineral carbonation to both natural silicates and industrial wastes, where the kinetics of the reaction is believed to more favourable, is ongoing. Moreover, an evaluation is needed to determine the fraction of the natural reserves of silicates, which greatly exceed the needs that can be effectively exploited for mineral carbonation. This will require a thorough study mapping the resources and matching sources and sinks, as in O'Connor et al. 2005. The actual size of the resource base will be significantly influenced by the legal and societal constraints at a specific location. Integrating power generation, mining, carbonation reaction, carbonates' disposal, and the associated transport of materials and energy, needs to be optimized, in a site-specific manner. A final important gap in mineral carbonation is the lack of a demonstration plant.

7.3 Industrial Uses of Carbon Dioxide and its Emissions' Mitigation Potential

7.3.1 Introduction

As an alternative to storing captured CO_2 in geological formations (see Chapter 5), in the oceans (see Chapter 6), or in mineral form as carbonates (see Chapter 7.2), this section of the report assesses the potential for reducing net CO_2 emissions to the atmosphere by using CO_2 either directly or as a feedstock in chemical processes that produce valuable carbon containing products. The utilization of CO_2 establishes an inventory of stored CO_2, i.e. the carbon chemical pool, primarily in the form of carbon-containing fuels, chemicals and other products (Xiaoding and Moulijn, 1996). The production and use of these products involves a variety of different "life cycles" (i.e., the chain of processes required to manufacture a product from raw materials, to use the product for its intended purpose, and ultimately to dispose of it or to reuse it in some fashion). Depending on the product life cycle, CO_2 is stored for varying periods of time and in varying amounts. As long as the recycled carbon remains in use, this carbon pool successfully stores carbon. Withdrawal from this pool, by decay or by disposal typically re-injects this carbon into the atmospheric pool.

CO_2 which has been captured using one of the options described in Chapter 3 could reduce net CO_2 emissions to the atmosphere if used in industrial processes as a source of carbon only if the following criteria are met:

1. The use of captured CO_2 must not simply replace a source of CO_2 that would then be vented to the atmosphere. Replacement of CO_2 derived from a lime kiln or a fermentation process would not lead to a net reduction in CO_2 emissions, while on the other hand replacement of CO_2 derived from natural geological deposits, which would thus be left undisturbed, would lead to a net reduction of CO_2 emissions. This would apply to the majority of the CO_2 used for enhanced oil recovery in the United States (see Section 5.3.2) that is currently provided from natural geological deposits (Audus et Oonk, 1997).
2. The compounds produced using captured CO_2 must have a long lifetime before the CO_2 is liberated by combustion or other degradation processes.
3. When considering the use of captured CO_2 in an industrial process the overall system boundary must be carefully defined to include all materials, fossil fuels, energy flows, emissions and products in the full chain of processes used to produce a unit of product in order to correctly determine the overall (net) CO_2 avoided.

CO_2 reductions solely due to energy efficiency improvements are not within the scope of this report which is focused on capture and storage rather than efficiency improvements. Similarly while environmental benefits like those obtained in replacing organic solvents with supercritical CO_2 may slightly increase the carbon chemical pool, these primary drivers are not discussed in this report. Similarly, this report specifically excludes all uses of captured CO_2 to replace other chemicals which are released into the atmosphere and which have high greenhouse gas potential, e.g. fluorocarbons. This area is covered by the IPCC/TEAP Special Report on Safeguarding the Ozone Layer and the Global Climate System: issues related to Hydrofluorocarbons and Perfluorocarbons (IPCC/TEAP, 2005).

The third point is especially important in any effort to estimate the potential for net CO_2 reductions from the substitution of a CO_2-utilizing process for alternative routes to manufacturing a desired product. In particular, it is essential that the system boundary encompass all "upstream" processes in the overall life cycle, and not focus solely on the final production process of interest. The appropriate system boundary is shown schematically in Fig. 7.4. This is an extension of the system boundary diagrams shown earlier in Section 7.2 (Figure 7.1) and in Chapter 1 (Figure 1.4) in the context of a CO_2 capture and storage system. The inputs include all fossil fuels together with all other materials used within the system. The fossil fuel input provides energy to the power or industrial plant, including the CO_2 capture system, as well as the elemental carbon used as building blocks for the new chemical compound. From the primary fuel-consuming processes, flows of CO_2, energy and materials pass to the industrial process which utilizes the captured CO_2. This produces a desired product (containing carbon derived from captured CO_2) together with other products (such as useful energy from the power plant) and environmental emissions that may include CO_2 plus other gaseous, liquid or solid residuals.

Once the overall system has been defined and analyzed in this way, it can also be compared to an alternative system that does not involve the use of captured CO_2. Using basic mass and energy balances, the overall avoided CO_2 can then be assessed as the difference in net emissions associated with the production of a desired product. In general, the difference could be either positive or negative, thus meaning that utilization of CO_2 could result in either a decrease or increase in net CO_2 emissions, depending on the details of the processes being compared. Note that only fossil fuels as primary energy source are considered in this framework; renewable energy sources and nuclear power are specifically excluded as their availability would have implications well beyond the analysis of CO_2 utilization options (see Chapter 8 for further discussion). Note too that other emissions from the process may include toxic or harmful materials, whose flows also could be either reduced or increased by the adoption of a CO_2-based process.

The application of this framework to the assessment of CO_2 utilization processes is discussed in more detail later in this chapter. First, however, we examine current uses of CO_2 in industrial processes and their potential for long-term CO_2 storage.

Figure 7.4. Material and energy balances through the system boundaries for a power plant or an industrial plant with CO_2 capture, followed by an industrial process using CO_2. The inputs include all fossil fuels together with all other materials used within the system. The fossil fuel input provides energy to the power or industrial plant, including the CO_2 capture system, as well as the elemental carbon used as building blocks for the new chemical compound. From the primary fuel-consuming processes, flows of CO_2, energy and materials pass to the industrial process, which utilizes the captured CO_2. This produces a desired product (containing carbon derived from captured CO_2) together with other products (such as useful energy from the power plant) and environmental emissions that may include CO_2 plus other gaseous, liquid or solid residuals.

7.3.2 Present Industrial Uses of Carbon Dioxide

Carbon dioxide is a valuable industrial gas with a large number of uses that include production of chemicals, e.g. urea, refrigeration systems, inert agent for food packaging, beverages, welding systems, fire extinguishers, water treatment processes, horticulture, precipitated calcium carbonate for the paper industry and many other smaller scale applications. Large quantities of carbon dioxide are also used for enhanced oil recovery, particularly in the United States (see Section 5.3.2.). Accordingly, there is a large technical literature dealing with CO_2 uses in industry, and active research groups exploring new or improved CO_2 utilization processes.

Much of the carbon dioxide used commercially is recovered from synthetic fertilizer and hydrogen plants, using either a chemical or physical solvent scrubbing system (see Section 3.5.2). Other industrial sources of CO_2 include the fermentation of sugar (dextrose) used to produce ethyl alcohol:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \qquad (3)$$

Industrial CO_2 is also produced from limekilns, such as those used in the production of sodium carbonate and in the Kraft wood pulping process. This involves the heating (calcining) of a raw material such as limestone:

$$CaCO_3 \rightarrow CaO + CO_2, \qquad (4)$$

In some parts of the world, such as the United States, Italy, Norway and Japan, some CO_2 is also extracted from natural CO_2 wells or recovered during the production and treatment of raw natural gas which often contains CO_2 as an impurity (see Chapter 2 for more details about CO_2 sources).

A large proportion of all CO_2 recovered is used at the point of production to make further chemicals of commercial importance, chiefly urea and methanol. The CO_2 recovered for other commercial uses is purified, liquefied, delivered and stored mostly as a liquid typically at 20 bar and -18°C (Pierantozzi, 2003).

Table 7.1 shows the worldwide production and CO_2 usage rates for the major chemicals or industrial applications currently using CO_2 (excluding enhanced oil recovery, which is dealt with on Chapter 5). Also shown is the approximate lifetime of the stored carbon before being degraded to CO_2 that is emitted to the atmosphere. Such values mean that the fraction of the CO_2 used to

produce the compounds in the different chemical classes or for the different applications, which is still stored after the period of time indicated in the last column of Table 7.1 drops to zero.

Table 7.1. Industrial applications of CO_2 (only products or applications at the megatonne-scale): yearly market, amount of used CO_2, its source, and product lifetime (Aresta and Tommasi, 1997; Hallman and Steinberg, 1999; Pelc *et al.*, 2005). The figures in table are associated with a large uncertainty.

7.3.3 New Processes for CO_2 Abatement

7.3.3.1 Organic Chemicals and Polymers

A number of possible new process routes for the production of chemicals and polymers have been considered in which CO_2 is used as a substitute for other C_1 building blocks, such as carbon monoxide, methane and methanol. The use of CO_2, which is an inert gas whose carbon is in a highly oxidised state, requires development of efficient catalytic systems and, in general, the use of additional energy for CO_2 reduction. Chemicals that have been considered include polyurethanes and polycarbonates where the motivation is primarily to avoid the use of phosgene because of its extreme toxicity rather than to find a sink for CO_2. The proposed processes can have a lower overall energy consumption than the current phosgene based routes leading to further CO_2 emission reductions. Current world consumption of polycarbonates is about 2.7 Mt/yr. If all polycarbonate production was converted to CO_2 based processes the direct consumption of CO_2 would be about 0.6 $MtCO_2$/yr. Some CO_2 savings are claimed for energy/materials changes in the process, which are difficult to quantify from current published data.

Similarly, if all world polyurethane production was converted, then direct CO_2 consumption would be about 2.7 $MtCO_2$/yr. However, little progress in commercial application of CO_2 based production has been reported. And as indicated earlier, these possible CO_2 applications directly affect only a very small fraction of the anthropogenic CO_2 emitted to the atmosphere. The net savings in CO_2 would be even smaller or could be negative, as the energy that was available in the hydrocarbon resource is missing in the CO_2 feedstock, and unless compensated for by improved process efficiency it would have to be made up by additional energy supplies and their associated CO_2 emissions.

7.3.3.2 Fuel Production using Carbon Dioxide

Liquid carbon based fuels, e.g. gasoline and methanol, are attractive because of their high energy density and convenience of use, which is founded in part on a well-established infrastructure. Carbon dioxide could become the raw material for producing carbon-based fuels with the help of additional energy. Since energy is conserved, this cannot provide a net reduction in carbon dioxide emissions as long as the underlying energy source is fossil carbon. If a unit of energy from a primary resource produces a certain amount of CO_2, then producing a fuel from CO_2 will recycle CO_2 but release an equivalent amount of CO_2 to provide the necessary energy for the conversion. Since all these conversion processes involve energy losses, the total CO_2 generated during fuel synthesis tends to exceed the CO_2 converted, which once used up is also emitted.

Production of liquid carbon-based fuels from CO_2 only reduces CO_2 emissions if the underlying energy infrastructure is not based on fossil energy. For example, one could still use gasoline or methanol rather than converting the transportation sector to hydrogen, by using hydrogen and CO_2 as feedstocks for producing gasoline or methanol. The hydrogen would be produced from water

using hydropower, or nuclear energy, or solar energy, or wind energy. As long as there remains some power generation using fossil fuels, carbon dioxide for this conversion will be available (Eliasson, 1994). Alternatively, it might be possible to create a closed cycle with CO_2 being retrieved from the atmosphere by biological or chemical means. Such cycles would rely, as the hydrogen economy would, on the availability of cheap, clean and abundant non-fossil energy, and as such they are beyond the scope of this report.

Methanol production is an example of the synthesis of liquid fuels from CO_2 and hydrogen. Today a mixture of CO, CO_2 and hydrogen is produced through reforming or partial oxidation or auto thermal reforming of fossil fuels, mainly natural gas. The methanol producing reactions, which are exothermic, take place over a copper/zinc/alumina catalyst at about 260°C (Inui, 1996; Arakawa, 1998; Ushikoshi *et al.*, 1998; Halmann and Steinberg, 1999):

$$CO + 2\ H_2 \leftrightarrow CH_3OH \quad (5)$$

$$CO_2 + 3\ H_2 \leftrightarrow CH_3OH + H_2O \quad (6)$$

Alternatively one could exploit just reaction (6), by using captured CO_2 and hydrogen from water hydrolysis powered for instance by solar energy (Sano *et al.*, 1998).

7.3.3.3 Capture of CO_2 in Biomass

Biomass production of fuels also falls into the category of generating fuels from CO_2. With the help of photosynthesis solar energy can convert water and CO_2 into energetic organic compounds like starch. These in turn can be converted into industrial fuels like methane, methanol, hydrogen or bio-diesel (Larson, 1993). Biomass can be produced in natural or agricultural settings, or in industrial settings where elevated concentrations of CO_2 from the off-gas of a power plant would feed micro-algae designed to convert CO_2 into useful chemicals (Benemann, 1997). Since biological processes collect their own CO_2, they actually perform CO_2 capture (Dyson, 1976). If the biomass is put to good use, they also recycle carbon by returning it to its energetic state. Biomass production eliminates the need for fossil fuels, because it creates a new generation of biomass-based carbonaceous fuels. As a replacement for fossil energy it is outside the scope of this report. As a CO_2 capture technology, biomass production is ultimately limited by the efficiency of converting light into chemically stored energy. Currently solar energy conversion efficiencies in agricultural biomass production are typically below 1% (300 GJ per hectar per year or 1 W/m^2; Larson, 1993). Micro-algae production is operating at slightly higher rates of 1 to 2% derived by converting photon utilization efficiency into a ratio of chemical energy per unit of solar energy (Melis *et al.*, 1998; Richmond and Zou, 1999). Hence the solar energy collection required for micro-algae to capture a power plant's CO_2 output is about one hundred times larger than the power plant's electricity output. At an average of 200 W/m^2 solar irradiation, a 100 MW power plant would require a solar collection area in the order of 50 km^2.

7.3.4 Assessment of the Mitigation Potential of CO_2 Utilization

This final section aims at clarifying the following points: (i) to what extent the carbon chemical pool stores CO_2; (ii) how long CO_2 is stored in the carbon chemical pool; (iii) how large the contribution of the carbon chemical pool to emissions' mitigation is.

To consider the first point, i.e. the extent of CO_2 storage provided by the carbon chemical pool, it is worth referring again to Table 7.1. As reported there, total industrial CO_2 use is approximately 115 $MtCO_2/yr$; production of urea is the largest consumer of CO_2, accounting for over 60 % of that total. To put it in perspective, the total is only 0.5 percent of total anthropogenic CO_2 emissions, i.e.

~24 Gt CO_2. However, it is essential to realize that these figures represent only the yearly CO_2 flux in and out of the carbon chemical pool, and not the actual size of such pool, which is controlled by marketing and product distribution considerations and might be rather smaller than the total yearly CO_2 consumption. Moreover, the contribution to the storage of carbon – on a yearly base for instance - does not correspond to the size of the pool, but to its size variation on a yearly base, or in general on its rate of change that might be positive (increase of carbon storage and reduction of CO_2 emissions) or negative (decrease of carbon storage and increase of CO_2 emissions) depending on the evolution of the markets and of the distribution systems (see also Box 7.2 for a quantitative example). Data on the amount of carbon stored as inventory of these materials in the supply chain and on the rate of change of this amount is not available, but the figures in Table 7.1 and the analysis above indicate that the quantity of captured carbon that could be stored is very small compared with total anthropogenic carbon emissions. Thus, the use of captured CO_2 in industrial processes could have only a minute (if any) effect on reduction of net CO_2 emissions.

As to the second point, i.e. the duration of CO_2 storage in the carbon chemical pool, typical lifetime of the CO_2 consuming chemicals, when in use before being degraded to CO_2, which is emitted to the atmosphere, are given in the last column of Table 7.1. Rather broad ranges are associated to classes of compounds constituted of a variety of different chemicals. The lifetime of the materials produced which could use captured CO_2 could vary from a few hours for a fuel such as methanol to a few months for urea fertilizer to decades for materials such as plastics and laminates, particularly those materials used in the construction industry. This indicates that even when there is a net storage of CO_2 as to the discussion in the previous paragraph, the duration of such storage is limited.

As to the last point, i.e. the extent of emissions' mitigation provided by use of captured CO_2 to produce the compounds in the carbon chemical pool, replacing in a chemical process carbon derived from a fossil fuel, e.g. a hydrocarbon, with captured CO_2 is sometimes possible, but does not affect the overall carbon budget, i.e. CO_2 does not replace the fossil fuel feedstock. The hydrocarbon has in fact two functions, i.e. it provides energy and it provides carbon as building block. The CO_2 fails to provide energy, since it finds itself at a lower energy level than the hydrocarbon (see Box 7.3). The energy of the hydrocarbon is often needed in the chemical process, and as in the production of most plastics it is embodied in the end product. Alternatively, the energy of the hydrocarbon is available and likely to be utilized in other parts of the process, e.g. purification, pre-treatment, or in other processes within the same plant. If this energy is missing since CO_2 is used as carbon source, it has to be replaced somehow to close the energy balance of the plant. As long as the replacement energy is provided from fossil fuels, net CO_2 emissions remain unchanged. It is worth noting that an economy with large non-fossil energy resources could consider CO_2 feed stocks to replace hydrocarbons in chemical synthesis. Such approaches are not covered here, since they are specific examples of converting to non-fossil energy, and as such are driven by the merits of the new energy source rather than by the need for capture and storage of CO_2.

7.3.5 Future Scope

The scale of the use of captured CO_2 in industrial processes is too small, the storage times too short, and the energy balance too unfavourable for industrial uses of CO_2 to become significant as a means of mitigating climate change. There is a lack of data available to adequately assess the possible overall CO_2 inventory of processes which involve CO_2 substitution, with associated energy balances and the effects of changes in other feed stocks and emissions. However, the analysis above demonstrates that, although the precise figures are difficult to estimate and even their sign is questionable, the contribution of these technologies to CO_2 storage is negligible. Research is

continuing on the use of CO_2 in organic chemical polymer and plastics production, but the drivers are generally cost, elimination of hazardous chemical intermediates and the elimination of toxic wastes, rather than the storage of CO_2.

Box 7.1. Wet Mineral Carbonation Process.

A comprehensive energy and economic evaluation of the single step wet carbonation process has been reported (O'Connor *et al*., 2005). Though limited to the specific carbonation process illustrated in Figure 7.3, this study is based on about 600 experimental tests and looks not only at the fundamental and technical aspects of the process but also at the matching of carbon dioxide sources and potential sinks that in this case are natural silicate deposits. In particular, seven large ultramafic ores in the USA have been considered (two olivines, four serpentines - three lizardites and one antigorite - and one wollastonite); three are located on the west coast, three on the east coast and one in Texas. The selection of the seven ores has also been based on considerations of regional coal consumption and potential CO_2 availability.

The three different minerals exhibit different reactivity, which is measured as the extent of the carbonation reaction after one hour under specified operating conditions. A trade off has been observed between extent of reaction and mineral pre-treatment, i.e. the higher reactivity is obtained for the more intense pre-treatment, which represents an energy cost. Mechanical activation is effective for the olivine and the wollastonite, and involves the use of both conventional rod and ball milling techniques with an energy consumption of up to about 100 kWh/ton mineral (standard pre-treatment), and ultra-fine grinding for up to more than 200 kWh/ton mineral (activated process). Conversion is no more than 60% in the former case, and up to above 80% in the latter. In the case of the serpentine, after milling (standard pre-treatment), thermal activation at 630°C is effective for the antigorite (up to 92% conversion) but only partially for the lizardite (maximum conversion not larger than 40%), and requires an energy consumption of about 350 kWh/ton mineral. Optimal operating conditions for this wet process are mineral dependent and correspond to 185°C and 15 MPa for the olivine, 155°C and 11.5 MPa for the heat treated serpentine, and 100°C and 4 MPa for the wollastonite. In the first two cases, the carbonation reaction takes place in the presence of 0.64 mol/L sodium bicarbonate and 1 mol/L sodium chloride.

Ore (type of pre-treatment)	Conversion after 1 hour [%]	Cost [$/ton ore]	Energy input[a] [kWh/t CO_2 stored]	Cost [$/t CO_2 stored]
Olivine (standard)	61	19	310	55
Olivine (activated)	81	27	640	59
Lizardite (standard)	9	15	180	430
Lizardite (activated)	40	44	180+2120=2300	210
Antigorite (standard)	62	15	180	250
Antigorite (activated)	92	48	180+830=1010	78
Wollastonite (standard)	43	15	190	91
Wollastonite (activated)	82	19	430	64

[a] The study assumes a coal fired power plant with 35% efficiency, corresponding to one ton of CO_2 released per 1000 kWh electricity. The equivalent heat value for the same coal input is then 2850 kWh. The two items in the sum break the total energy input into electrical + thermal; in all other cases it is pure electrical energy.

Process costs have been calculated for these seven ores in the case of both standard mineral pre-

treatment and activated process. Costs include only storage, i.e. neither CO_2 capture nor CO_2 transport, and are based on the assumption that CO_2 is received pure at 15 MPa at the plant. Investment costs are calculated accounting for the different reactor costs depending on the different operating conditions corresponding to the different mineral ores. Storage costs are calculated per ton of silicate ore and per ton of CO_2 stored, and are complemented by the energy consumption per ton of CO_2 stored in the Table below. The table highlights a trade off between energy input associated to the pre-treatment procedure and cost per unit carbon dioxide stored. Assuming that the cheapest technology is used for each mineral, costs range from 55 \$/t CO_2 stored for olivine (standard pre-treatment), to 64 \$/t CO_2 stored for wollastonite (activated), to 78 \$/t CO_2 stored for antigorite (activated), to 210 \$/t CO_2 stored for lizardite (activated). Since the last case requires too large an energy input, the cost of the most realistic technologies falls into a range from 50 to 100 \$/t CO_2 stored.

Box 7.2. Carbon Chemical Pool.

The carbon chemical pool is the ensemble of anthropogenic carbon containing organic chemicals. This box aims at providing criteria how to quantify the quantitative impact on carbon mitigation of such a pool. If this impact were significant, using carbon from CO_2 could be an attractive storage option for captured CO_2.

Let us consider a specific chemical A, whose present worldwide production is 12 Mt/y, whose worldwide inventory is 1 Mt, i.e. the monthly production, and whose lifetime before degradation to CO_2 and release to the atmosphere is less than one year.

If next year production and inventory of A do not change, the contribution to CO_2 storage of this member of the chemical pool will be null. If production increased by a factor ten to 120 Mt/y, whereas inventory were still 1 Mt, again the contribution of A to CO_2 storage would be null.

If on the contrary next year production increases, and inventory also increases, e.g. to 3 Mt, to cope with increased market demand, the contribution of A to CO_2 storage over the year will be equivalent to the amount of CO_2 stoichiometrically needed to produce 2 Mt of A. However, if due to better distribution policies and despite increased production, the worldwide inventory of A decreased to 0.7 Mt, then A would yield a negative contribution to CO_2 storage, i.e. over the year the amount of CO_2 stoichiometrically needed to produce 0.3 Mt of A would be additionally emitted to the atmosphere.

Therefore, the impact on carbon dioxide mitigation of the carbon chemical pool does not depend on the amounts of carbon containing chemical products produced; there is CO_2 emission reduction in a certain time only if the pool has grown during that time. In the presence of an increasing production, such impact can be positive or negative, as shown above. It is anyhow clear that since this would be a second or third order effect with respect to the overall production of carbon containing chemicals, which is itself much smaller in terms of fossil fuel consumption than fossil fuel combustion, this impact will be rather insignificant with respect to the scale of the challenge carbon dioxide capture and storage technologies have to confront.

Box 7.3. Energy Gain or Penalty in using CO_2 as a Feedstock instead of Carbon.

CO_2 can be used as a provider of carbon atoms for chemical synthesis, as an alternative to standard processes where the carbon atom source is fossil carbon, as either coal or methane or other. This includes processes where the carbon atom in the CO_2 molecule either is reduced by providing energy, e.g. methanol synthesis, or does not change its oxidation state and does not need energy, e.g. synthesis of polycarbonates.

For the sake of simplicity let us consider a reaction from carbon to an organic final product A (containing n carbon atoms) that takes place in a chemical plant (standard process):
(1) nC -> A
Let us also consider the alternative route whereby CO_2 captured from the power plant, where carbon has been burnt, is used in the chemical plant where the synthesis of A is carried out; in this case the sequence of reactions would be:
(2) nC -> nCO_2 -> A

The overall energy change upon transformation of C into A, ΔH, is the same in both cases. The difference between the two cases is that in case (2) this overall energy change is split in two parts, i.e. $\Delta H=\Delta H_{com}+\Delta H_{syn}$, namely one for combustion in the power plant and the other for the synthesis of A from CO_2 in the chemical plant (ΔH_{com} will be -400 kJ/mol C, which means 400 kJ/mol are made available by the combustion of carbon). If ΔH is negative, i.e. an overall exothermic reaction (1), then ΔH_{syn} will be either negative or even positive. If ΔH is positive, i.e. an overall endothermic reaction (1), then ΔH_{syn} will be even more positive. In both cases, i.e. exothermic or endothermic reaction, the chemical plant will lack 400 kJ/mol C energy in case (2) with respect to case (1). This energy has already been exploited in the power plant and is not available in the chemical plant any more. It is worth noting that large scale chemical plants (these are those of interest for the purpose of carbon dioxide emission mitigation) make the best possible use of their energy, by applying so called heat integration, i.e. by optimizing energy use through the whole plant and not just for individual processes. In case (1) chemical plants make good use of the 400 kJ/mol C that are made available by the reaction (1) in excess of the second step of reaction (2).

Therefore, in terms of energy there is no benefit in choosing path (2) rather than path (1). In terms of efficiency of the whole chemical process there might be a potential improvement, but there might also be a potential disadvantage, since route (1) integrates the heat generation associated to the oxidation of carbon and the conversion to product A. These effects are of second order importance and have to be evaluated on a case by case basis. Nevertheless, the scale of the reduction in CO_2 emissions would be rather small, since it would be even smaller than the scale of the production of the chemicals that might be impacted by the technology change, i.e. by the change from path (1) to path (2) (Audus and Oonk, 1997).

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Tables

Table 7.1. Industrial applications of CO_2 (only products or applications at the megatonne-scale): yearly market, amount of used CO_2, its source, and product lifetime (Aresta and Tommasi, 1997; Hallman and Steinberg, 1999; Pelc *et al.*, 2005). The figures in table are associated with a large uncertainty.

Chemical Product Class or Application	Market per year (Mt)	Amount of CO_2 used per year (Mt)	Source of CO_2	Lifetime[b]
Urea	90	65	Industrial	Six months
Methanol (additive to CO)	24	<8	Industrial	Six months
Inorganic carbonates	8	3	Industrial, Natural[a]	Decades to centuries
Organic carbonates	2.6	0.2	Industrial, Natural[a]	Decades to centuries
Polyurethanes	10	<10	Industrial, Natural[a]	Decades to centuries
Technological	10	10	Industrial, Natural[a]	Days to years
Food	8	8	Industrial, Natural[a]	Months to years

[a] Natural sources include both geological wells and fermentation

[b] The fraction of used CO_2 that is still stored after the indicated period of time drops to zero.

Figures

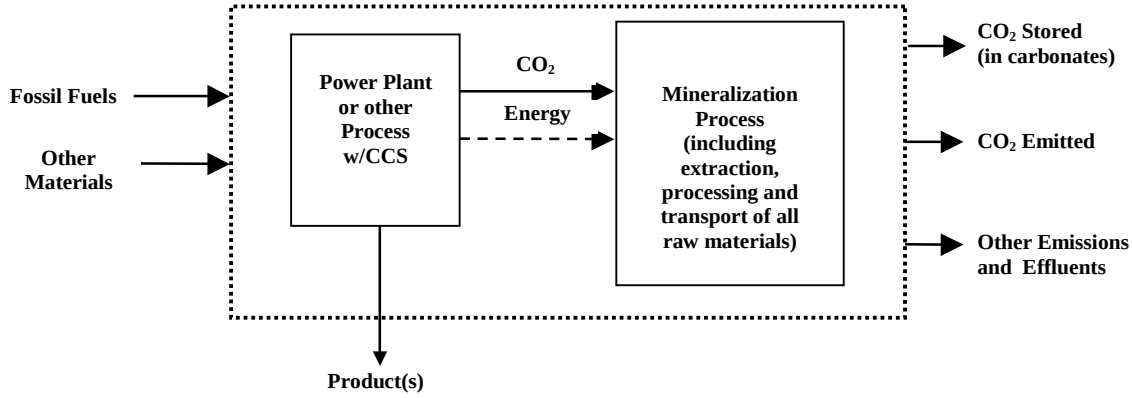

Figure 7.1. Material and energy balances through the system boundaries for a power plant with CO_2 capture and storage through mineral carbonation. The fossil fuel input provides energy both to the power plant that produces CO_2, and to the mineralization process (either directly or indirectly via the power plant). The "other materials" input serves all processes within the system boundaries and includes the metal oxide bearing materials for mineralization. The "other emissions" output is made up of the by-products of the mineralization reaction, i.e. silica and possibly water, as well as of non-reacted input materials.

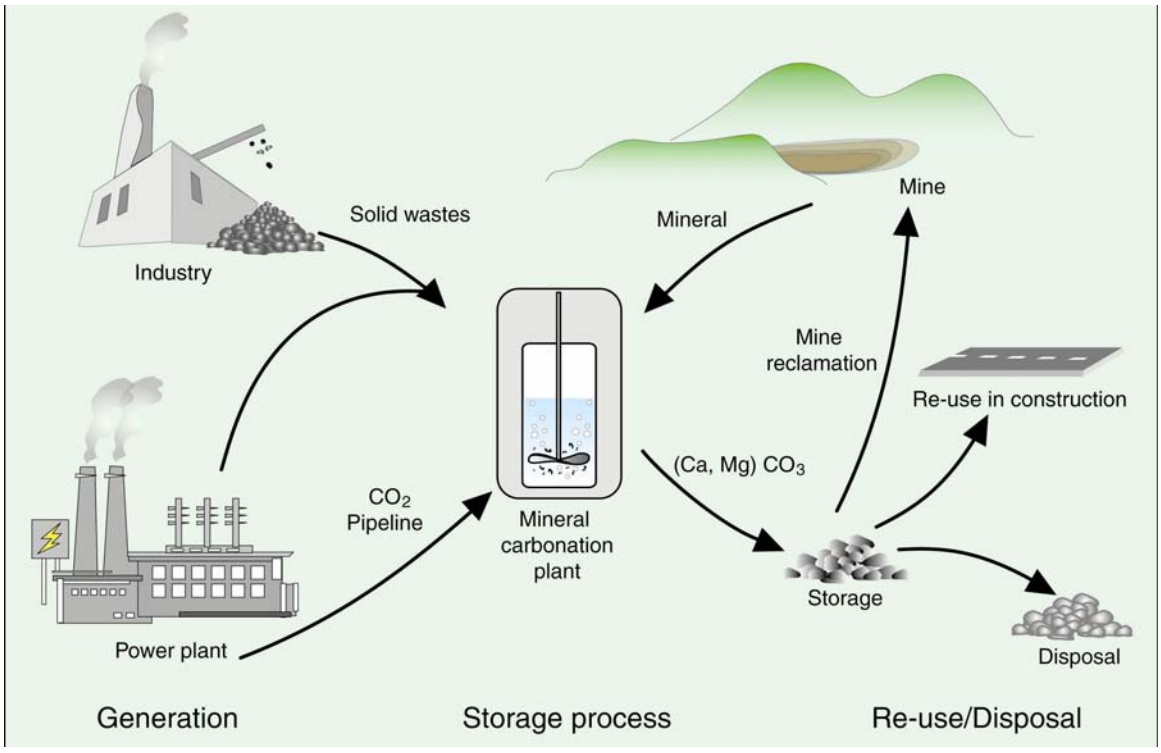

Figure 7.2. Material fluxes and process steps associated to the *ex-situ* mineral carbonation of silicate rocks or industrial residues (Courtesy Energy Research Centre of the Netherlands (ECN)).

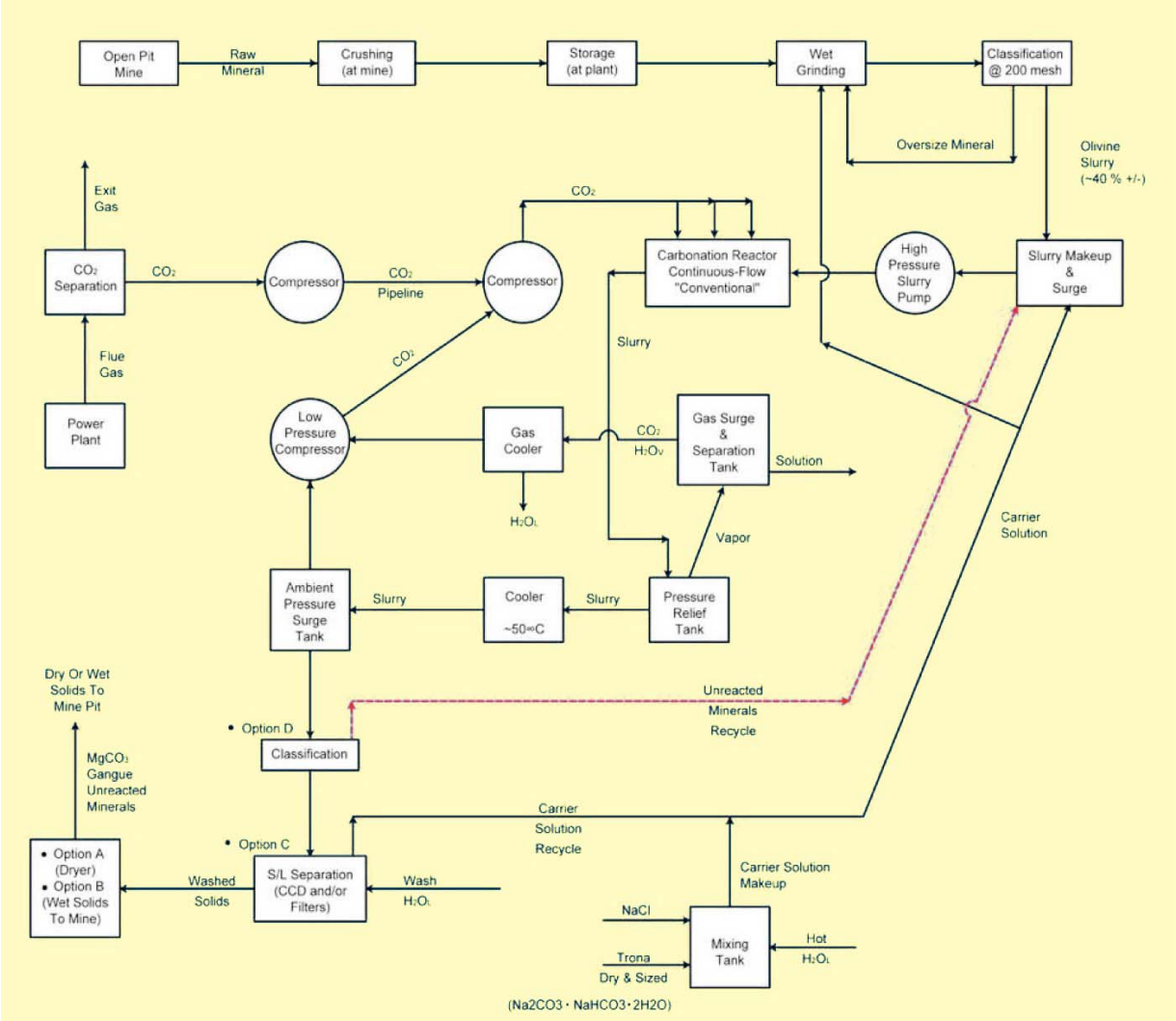

Figure 7.3. Process scheme of the single step mineral carbonation of olivine in aqueous solution (courtesy Albany Research Centre). "Single step" indicates that mineral dissolution and carbonate precipitation take place simultaneously in the same carbonation reactor, whereas more steps are of course needed for the whole process including preparation of the reactants and separation of the products.

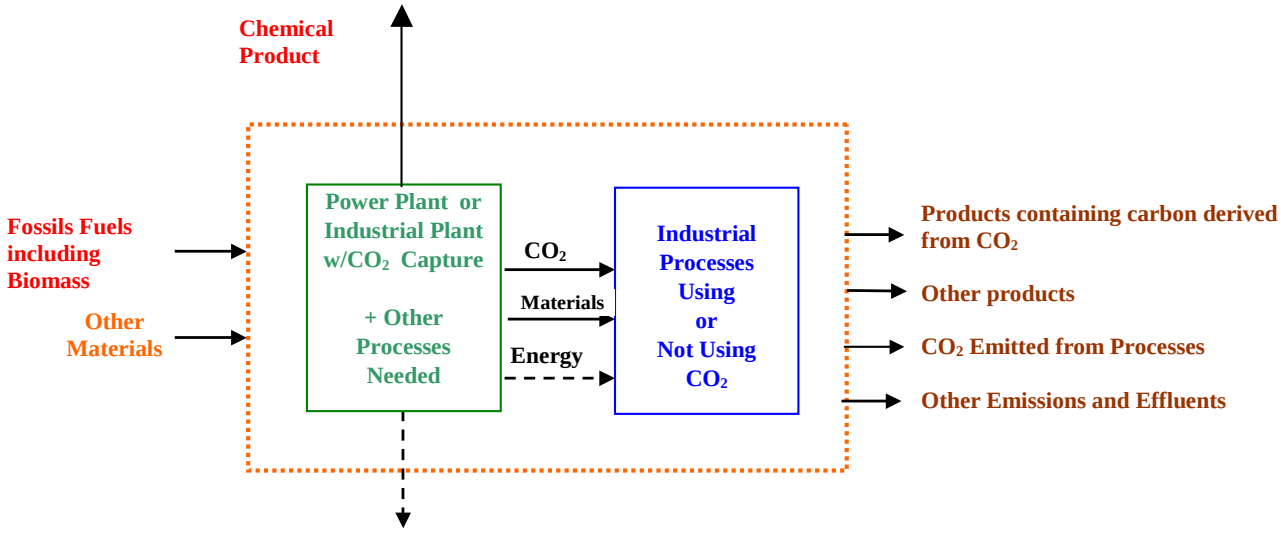

Figure 7.4. Material and energy balances through the system boundaries for a power plant or an industrial plant with CO_2 capture, followed by an industrial process using CO_2. The inputs include all fossil fuels together with all other materials used within the system. The fossil fuel input provides energy to the power or industrial plant, including the CO_2 capture system, as well as the elemental carbon used as building blocks for the new chemical compound. From the primary fuel-consuming processes, flows of CO_2, energy and materials pass to the industrial process which utilises the captured CO_2. This produces a desired product (containing carbon derived from captured CO_2) together with other products (such as useful energy from the power plant) and environmental emissions that may include CO_2 plus other gaseous, liquid or solid residuals.

8. Costs and economic potential

Coordinating Lead Authors
HOWARD HERZOG (UNITED STATES), KOEN SMEKENS (BELGIUM)

Lead Authors
Pradeep Dadhich (India), James Dooley (United States), Yasumasa Fujii (Japan), Olav Hohmeyer (Germany), Keywan Riahi (Austria)

Contributing Authors
Makoto Akai (Japan), Chris Hendriks (Netherlands), Klaus Lackner (United States), Ashish Rana (India), Edward Rubin (United States), Leo Schrattenholzer (Austria), Bill Senior (United Kingdom)

Review Editors
John Christensen (Denmark), Greg Tosen (South Africa)

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Executive Summary

The major components of a carbon dioxide capture and storage (CCS) system include capture (separation plus compression), transport, and storage (including measurement, monitoring and verification). In one form or another, these components are commercially available; however, there is relatively little commercial experience in configuring all of these components into fully integrated CCS systems at the kinds of scales which would likely characterize their future deployment. The literature reports a fairly wide range of costs for employing CCS systems with fossil-fired power production and various industrial processes. The range spanned by these cost estimates is driven primarily by variability due to site specific considerations such as the technology characteristics of the power plant or industrial facility, the specific characteristics of the storage site, and the required transportation distance of carbon dioxide (CO_2). In addition there is uncertainty in estimates of future performance of capture, transport, storage, measurement and monitoring system components. The literature reflects a widely held belief that the cost of building and operating CO_2 capture systems should be reduced over time through technological advance.

The cost of employing a full CCS system for electricity generation from a fossil-fired power plant is dominated by the cost of capture. The application of capture technology would add about 1.8 to 3.4 US$ct/kWh to the cost of electricity from a pulverized coal power plant, 0.9 to 2.2 US$ct/kWh to the cost for electricity from an integrated gasification combined cycle coal power plant, and 1.2 to 2.4 US$ct/kWh from natural gas combined cycle power plant. Transportation and storage costs would add between -1 to 1 US$ct/kWh to this range for coal plants, and about half as much for gas plants. The negative costs are associated with assumed offsetting revenues from CO_2 storage in enhanced oil recovery (EOR) or enhanced coal bed methane (ECBM) projects. Typical costs for transportation and geological storage from coal plants would range from 0.05-0.6 US$ct/kWh. CCS technologies can also be applied to other industrial processes, such as hydrogen (H_2) production. In some of these non-power applications, the cost of capture is lower than for capture from fossil fired power plants, but as these sources are very diverse in concentration and partial pressure of CO_2 in the flue gases, the costs show a very broad range as well. In addition to fossil-based energy conversion processes, CCS may be applied to biomass-fed energy systems to create useful energy (electricity or transportation fuels). The product cost of these systems is very sensitive to the potential price of the carbon permit and the associated credits via the systems resulting negative emissions. These systems can be fuelled solely by biomass, or biomass can be co-fired in conventional coal-burning plants, in which case the quantity is normally limited to about 10-15% of the energy input.

Energy and economic models are used to study future scenarios concerning CCS deployment and costs. These models indicate that CCS systems are unlikely to deploy on a large scale in the absence of an explicit policy that substantially limits greenhouse gas emissions to the atmosphere. The literature and current industrial experience indicates that in the absence of measures to limit CO_2 emissions there are only small, niche opportunities for CCS technologies to deploy. These early opportunities for CCS deployment likely centring on CO_2 captured from a high purity, low cost source and used for a value added application such as EOR or ECBM production, could provide valuable early experience with CCS deployment including creating parts of the infrastructure and knowledge base needed for future large-scale deployment of CCS systems.

With greenhouse gas emission limits imposed, many integrated assessment analyses indicate that CCS systems will be competitive with other large-scale mitigation options, such as nuclear power and renewable energy technologies. Most energy and economic modelling done to date suggests that CCS systems begin to deploy at a significant level when carbon prices begin to reach

approximately 25 - 30 US$/tCO$_2$ (90 - 110 US$/tC). They foresee CCS systems deploying on a large-scale within a few decades from the start of any significant global warming mitigation regime. The literature indicates that deployment of CCS systems will be higher the more stringent the modelled emission reduction regime is. Least cost CO$_2$ concentration stabilization scenarios, that also take into account economic efficiency of the system, model a progressively more constraining emissions mitigation over time. Most analyses indicate that notwithstanding significant penetration of CCS systems by 2050, the majority of CCS deployment will occur in the second half of this century. They also indicate early CCS deployment occurring in the industrialized nations but with deployment eventually spreading worldwide. While different scenarios vary the quantitative mix of technologies needed to satisfy the modelled emissions constraint, a consensus of the literature shows that CCS could be an important component of a broad portfolio of energy technologies and emission reduction approaches. In addition, CCS technologies are viewed as being compatible with the deployment of other potentially important long-term greenhouse gas mitigation technologies such as H$_2$ production from biomass and fossil fuels.

Published estimates of the global cumulative amount of CO$_2$ possibly being stored over the course of this century in the ocean as well as various geological formations for CO$_2$ stabilization scenarios between 450-750 ppmv span a wide range, from very small contributions to thousands of gigatons of CO$_2$. This wide range is to a large extent due to the uncertainty of long-term socio-economic, demographic and technological change, the main drivers of future CO$_2$ emissions. However, it is important to note that the majority of stabilization scenarios from 450-750 ppmv tend to cluster in the range of 220-2200 GtCO$_2$ (60-600 GtC). This demand for CO$_2$ storage appears to be within global estimates of total CO$_2$ storage capacity. The actual use of CCS is likely to be lower than the estimates for economic potential indicated by these energy and economic models, as there are other barriers to technology development not adequately accounted for in these modelling frameworks. Examples include concerns about environmental impacts, lack of a clear legal framework and uncertainty as to how quickly learning-by-doing will lower costs. This chapter closes with a section of Knowledge Gaps that would help to improve the fidelity of these model results.

Given the potential for hundreds to thousands of gigatonnes of CO$_2$ to be stored in various geological formations and the ocean, questions have been raised about the implications of gradual leakage from these reservoirs. From an economic perspective, such leakage - if it were to occur - can be thought of as another potential future CO$_2$ emissions source, with the cost of offsetting this leaked CO$_2$ being equal to the cost of emission offsets in the year in which the previously stored CO$_2$ is released to the atmosphere. Within this purely economic framework, the few studies that have looked at this topic indicate that some CO$_2$ leakage can be accommodated while still making progress towards the goal of stabilizing atmospheric concentrations of CO$_2$.

8.1 Introduction

In this chapter, we address two of the key questions regarding any CO$_2$ mitigation technology: "How much will it cost?" and "How do CCS technologies fit into a portfolio of greenhouse gas mitigation options?" There are no simple answers to these questions. Costs for CCS technologies depend on many factors: fuel prices, the cost of capital, costs for meeting potential regulatory requirements like monitoring to just name a few. Add to this the uncertainties associated with technology development, the resource base for storage potential, the regulatory environment, etc., it becomes obvious why there are many answers to what appear to be simple questions.

This chapter starts (Section 8.2) by looking at the costs of the system components, namely capture and compression, transport, and storage (including monitoring costs and by-product credits from

operations such as EOR). There are commercial operations associated with each of these components, which provides a basis for the assessment of current costs. While more uncertain, an assessment is also included for how these costs will change in the future. The chapter next reviews the findings from economic modelling efforts (Section 8.3). These models start with the component costs in various degrees of aggregation and then model how the costs change with time and how CCS technologies compete with other CO_2 mitigation options under a variety of economic and policy assumptions. The chapter concludes by examining the economic implications of different storage times (Section 8.4) and summarizing the encountered gaps in knowledge (Section 8.5).

8.2 Component Costs

This section presents cost summaries for the three key components of a CCS system, namely capture (including compression), transport, and storage. Sections 8.2.1-8.2.3 contain a summary of results from Chapters 3-7. Readers are referred to those chapters for more details concerning the component costs. Results are presented here in a form most convenient for each section. Transport costs are given in US$/t$CO_2$/km, while storage costs in US$/t$CO_2$ stored. Capture costs for different types of power plants are represented as an increase in the electricity generation cost (US$/MWh). A discussion of how one integrates the costs of capture, transport and storage for a particular system into a single value is presented in Section 8.2.4.

8.2.1 Capture and Compression[1]

For most large sources of CO_2 (e.g., power plants), the cost of capturing CO_2 is the largest component of overall CCS costs. In this report, capture costs include the cost of compressing the CO_2 to a pressure suitable for pipeline transport (typically about 14 MPa). However, the cost of any additional booster compressors that may be needed is included in the cost of transport and/or storage.

The total cost of CO_2 capture includes the additional capital requirements plus added operating and maintenance costs incurred for any particular application. For current technologies, a substantial portion of the overall cost is due to the energy requirements for capture and compression. As elaborated in Chapter 3, a large number of technical and economic factors related to the design and operation of both the CO_2 capture system and the power plant or industrial process to which it is applied influence the overall cost of capture. For this reason, the reported costs of CO_2 capture vary widely, even for similar applications.

Table 8.1. Summary of new plant performance and CO_2 capture cost based on current technology.

Table 8.1 summarizes the CO_2 capture costs reported in Chapter 3 for baseload operations of new fossil fuel power plants (in the size range of 300-800 MW) employing current commercial technology. The most widely studied systems are new power plants based on coal combustion or gasification. For costs associated with retrofitting existing power plants, see Table 3.8. For a modern (high-efficiency) coal-burning power plant, CO_2 capture using an amine-based scrubber increases the cost of electricity generation (COE) by approximately 40 to 70 percent while reducing CO_2 emissions per kilowatt-hour (kWh) by about 85%. The same CO_2 capture technology applied to a new natural gas combined cycle (NGCC) plant increases the COE by approximately 40 to 70 percent. For a new coal-based plant employing an integrated gasification combined cycle (IGCC) system, a similar reduction in CO_2 using current technology (in this case, a water gas shift reactor

[1] This section is based on material presented in Section 3.7. The reader is referred to that section for a more detailed analysis and literature references.

followed by a physical absorption system) increases the COE by 20 to 55 percent. The lower incremental cost for IGCC systems is due in large part to the lower gas volumes and lower energy requirements for CO_2 capture relative to combustion-based systems. It should be noted that due to the absence of industrial experience with large-scale capture of CO_2 in the electricity sector, these numbers are subject to uncertainties, as is explained in Section 3.7.

Studies indicate that in most cases IGCC plants are slightly higher in cost without capture and slightly lower in cost with capture than a similarly sized PC plant fitted with a CCS system. On average, NGCC systems have a lower COE than both types of new coal-based plants with or without capture for baseload operation. However, the COE for each of these systems can vary markedly due to regional variations in fuel cost, plant utilization, and a host of other parameters. NGCC costs are especially sensitive to the price of natural gas, which has risen significantly in recent years. Thus, comparisons of alternative power system costs require a particular context to be meaningful.

For existing (combustion-based) power plants, CO_2 capture can be accomplished by retrofitting an amine scrubber to the existing plant. However, a limited number of studies indicate that the post-combustion retrofit option is more cost-effective when accompanied by a major rebuild of the boiler and turbine to increase the efficiency and output of the existing plant by converting it to a supercritical unit. For some plants, similar benefits can be achieved by repowering with an IGCC system that includes CO_2 capture technology. The feasibility and cost of any of these options is highly dependent on site-specific circumstances, including the size, age and type of unit, and the availability of space to accommodate a CO_2 capture system. A systematic comparison of the feasibility and cost of alternative retrofit and repowering options for existing plants, as well as the potential for more cost-effective options employing advanced technology such as oxyfuel combustion, is still missing.

Table 8.1 also illustrates the cost of CO_2 capture in the production of H_2, a commodity used extensively today for fuels and chemical production, but also widely viewed as a potential energy carrier for future energy systems. Here, the cost of CO_2 capture is mainly due to the cost of CO_2 compression, since separation of CO_2 is already carried out as part of the H_2 production process. For current processes, the cost of CO_2 capture adds approximately 5 to 30 percent to the cost of the H_2 product, according to recent studies.

In addition to fossil-based energy conversion processes, CO_2 could also be captured in power plants fuelled with biomass. At present, biomass plants are small in scale (<100 MW_e). Hence, the resulting costs of capturing of CO_2 are relatively high compared to fossil alternatives. For example, the capturing of 0.19 $MtCO_2$/yr in a 24 MW_e biomass IGCC plant is estimated to be about 82 US$/$tCO_2$ (300 US$/tC), corresponding to an increase of the electricity costs due to capture of about 80 US$/MWh (Audus and Freund, 2004). Similarly, CO_2 could be captured in biomass fuelled H_2 plants. The cost is reported to be between 22-25 US$/$tCO_2$ (80-92 US$/tC) avoided, in a plant producing 1 million Nm^3/d of H_2 (Makihira *et al.*, 2003). This corresponds to an increase in the H_2 product costs of about 2.7 US$/GJ (i.e, 20% of the H_2 costs without CCS). The competitiveness of biomass CCS systems is very sensitive to the value of CO_2 emission reductions, and the associated credits via the systems resulting negative emissions. Moreover, significantly larger biomass plants could potentially benefit from economies of scale, bringing down costs of the CCS systems to broadly similar levels as coal plants. However, so far there has been too little experience with large-scale biomass plants, so that their feasibility has not been proven yet, and their costs are difficult to estimate.

CCS technologies can also be applied to other industrial processes. Since these other industrial processes produce off gases that are very diverse in pressure and CO_2 concentration, the costs show a very broad range. In some of these non-power applications where a relatively pure CO_2 stream is produced as a by-product of the process (e.g., natural gas processing, ammonia production), the cost of capture is significantly lower than capture from fossil fuel fired power plants. In other processes like cement or steel production, capture costs are similar or even higher than capture from fossil fuel fired power plants.

New or improved technologies for CO_2 capture, combined with advanced power systems and industrial process designs, can significantly reduce the cost of CO_2 capture in the future. While there is considerable uncertainty about the magnitude and timing of future cost reductions, studies suggest that improvements to current commercial technologies can lower CO_2 capture costs by at least 20-30%, while new technologies currently under development offer the potential for more substantial cost reductions in the future. Previous experience indicates that realization of future cost reductions require sustained R&D together with deployment and adoption of commercial technologies.

8.2.2 Transport[2]

The most common and usually the most economical method to transport large amounts of CO_2 is through pipelines. A cost competitive way of transport over longer distances at sea might be the use of large tankers.

The three major cost elements for pipelines are construction costs (e.g., material, labour, possible booster station), operation and maintenance costs (e.g., monitoring, maintenance, possible energy costs) and other costs (e.g., design, insurance, fees, right-of-way). Special land conditions, like heavily populated areas, protected areas such as national parks, or crossing major waterways, may have significant impact on the costs. Offshore pipelines are about 40% to 70% more costly than equally sized onshore pipes. Pipeline construction is considered a mature technology and the literature does not foresee many cost reductions.

Figure 8.1. CO_2 transport costs range for onshore and offshore pipelines per 250 km, 'normal' terrain conditions. Indicated are high (solid lines) and low range (dotted lines). Data based on various sources (for details see Chapter 4).

Figure 8.1 depicts transport costs for 'normal' terrain conditions. Note that economies of scale dramatically reduce the cost, but that transportation in mountainous or densely populated areas could increase cost.

An alternative means of transport is by ship. For ship transport, the major cost elements are ships (or ship charter costs), loading and unloading facilities, intermediate storage facilities, harbour fees, and bunker fuel. The construction costs of large special purpose CO_2 tankers are not accurately known since none have been built to date. Based on preliminary designs, costs of CO_2 tankers are estimated at US$ 34 million for 10,000 tonne-sized ship, US$ 58 million with a capacity of 30,000 tonne, or US$ 82 million with a capacity of 50,000 tonne.

To transport 6 $MtCO_2$ per year a distance of 500 km by ship would cost about 10 US$/$tCO_2$ (37 US$/tC) or 5 US$/tCO_2/250km (18 US$/tC/250km). However, since the cost is relatively

[2] This section is based on material presented in Section 4.6. The reader is referred to that section for a more detailed analysis and literature references.

insensitive to distance, transporting the same 6 $MtCO_2$ a distance of 1250 km would cost about 15 US$/$tCO_2$ (55 US$/tC) or 3 US$/tCO_2/250km (11 US$/tC/250km), similar to the cost of pipeline transport). This illustrates the point that ship transport becomes cost-competitive to pipeline transport if CO_2 needs to be transported over larger distances. However, the break-even point beyond which ship transportation becomes cheaper than pipeline transportation is not simply a matter of distance alone, but involves many other aspects.

8.2.3 Storage

8.2.3.1 Geological storage[3]

Because the technologies and equipment used for geological storage are widely used in the oil and gas industries the cost estimates can be made with confidence. However, there will be a significant range and variability of costs due to site specific factors, onshore versus offshore, the reservoir depth and the geological characteristics of the storage formation (e.g., permeability, thickness, etc.). Representative estimates of the cost for storage in saline formations and disused oil and gas fields (see Table 8.2) are typically between 0.5-8.0 US$/$tCO_2$ (2-29 US$/tC) stored as detailed in Section 5.9.3. The lowest storage costs are for onshore, shallow, high permeability reservoirs and/or where wells and infrastructure in disused oil and gas fields may be reused.

The full range of cost estimates for individual options is very large. Storage monitoring cost information is currently limited, but is estimated to add 0.1-0.3 US$/$tCO_2$ (0.4-1.1 US$/tC) stored. Any well remediation and long-term liabilities are not included in these estimates. The costs of storage monitoring will depend on which technologies are used for how long, regulatory requirements and how long-term monitoring strategies evolve.

When storage is combined with EOR, enhanced gas recovery (EGR) or ECBM the benefits of enhanced production can offset some of the capture and storage costs. Onshore EOR operations have paid in the range of 10-16 US$/$tCO_2$ (37-59 US$/tC) for CO_2. The economic benefit of the enhanced production is strongly dependent on oil and gas prices. It should be noted that most of the literature basis for this report did not take into account the rise in oil and gas prices that started in 2003. For example, oil at 50 US$/barrel could justify a credit of 30 US$/$tCO_2$ (110 US$/tC). The economic benefits from enhanced production make EOR and ECBM potential early cost-effective options for geological storage.

Table 8.2. Estimates of CO_2 storage costs.

8.2.3.2 Ocean storage[4]

The cost of ocean storage is a function of both distance offshore and injection depth. Cost components include offshore transportation and injection of the CO_2. Various schemes for ocean storage have been considered, including:

- Using a tanker to transport low temperature (-55 to -50°C), high pressure (0.6-0.7 MPa) liquid CO_2 to a platform, from which it could be released through a vertical pipe to a depth of 3000 m.
- Using a carrier ship to transport liquid CO_2 with injection through a towed pipe from a moving dispenser ship

[3] This section is based on material presented in Section 5.9. The reader is referred to that section for a more detailed analysis and literature references.

[4] This section is based on material presented in Section 6.9. The reader is referred to that section for a more detailed analysis and literature references.

- Using an undersea pipeline to transport CO_2 to an injection site.

Costs are summarized in Table 8.2 for transport distances of 100-500 km offshore and an injection depth of 3000 m.

Chapter 6 also discusses the option of carbonate neutralization, where flue gas CO_2 is reacted with sea water and crushed limestone. The resulting mixture is then released into the upper ocean. The cost of this process has not been adequately addressed in the literature and therefore the possible cost of employing this process is not addressed here.

8.2.3.3 Storage via mineral carbonation[5]

Mineral carbonation is still in its R&D phase making costs uncertain. Costs include conventional mining and chemical processing. Mining costs include ore extraction, crushing and grinding, mine reclamation and disposal of tailings and carbonates. These are conventional mining operations and several studies estimated the cost at or below 10 US$/t$CO_2$ (36 US$/tC). Since this cost is based on similar mature and efficient operations, this puts a strong lower limit on the cost of mineral storage. Carbonation costs include chemical activation and carbonation. Translating today's laboratory implementations into industrial practice yields rough cost estimates around 50-100 US$/t$CO_2$ (180-370 US$/tC) stored. Costs and energy penalties (30 - 50% of the power plant output) are dominated by the activation of the ore necessary to accelerate the carbonation reaction. For mineral storage to become practical, additional research must reduce the cost of the carbonation step by a factor of three to four and eliminate a significant portion of the energy penalty by, for example, harnessing as much as possible the heat of carbonation.

8.2.4 Integrated systems

The component costs given in this section provide a foundation from which integrated system costs can be calculated. However, the cost to mitigate CO_2 emissions cannot be calculated simply by summing up the component costs for capture, transport and storage in units of "US$/t$CO_2$". This is because the amount of CO_2 captured will be different from the amount of atmospheric CO_2 emissions "avoided" while producing a given amount of a useful product (e.g., a kilowatt-hour of electricity or a kilogram of H_2). Thus, any cost expressed per tonne of CO_2 should be clearly defined as to its basis, e.g., either a *captured* basis or an *avoided* basis (see Box 8.1). The mitigation cost is best represented by the avoided cost basis. Table 8.3 presents ranges of total avoided costs for CO_2 capture, transport, and storage from four types of sources.

Box 8.1. Defining avoided costs for a fossil fuel power plant.

In general, the capture, transport, and storage of CO_2 require energy inputs. For a power plant, this means that amount of fuel input (and therefore CO_2 emissions) increases per unit of net power output. As a result, the amount of CO_2 produced per unit of product (e.g., a kWh of electricity) is greater for the power plant with CCS then the reference plant, as shown graphically in the diagram below. To determine the CO_2 reductions one can attribute to CCS, one needs to compare CO_2 emissions of the plant with capture to those of the reference plant without capture. These are termed the avoided emissions. Unless the energy requirements for capture and storage are zero, the amount of CO_2 avoided is always less than the amount of CO_2 captured. Hence the cost in US$/tonne avoided is greater than the cost in US$/tonne captured.

[5] This section is based on material presented in Section 7.2. The reader is referred to that section for a more detailed analysis and literature references.

Figure 8.2. Difference between CO_2 captured and CO_2 avoided.

Table 8.3a. Range of total costs for CO_2 capture, transport, and geological storage based on current technology for new power plants.

Table 8.3b. Range of total costs for CO_2 capture, transport, and geological storage based on current technology for a new H_2 production plant.

The mitigation costs (US$/t$CO_2$ avoided) reported in Table 8.3 are context specific and depend very much on what is chosen as a reference plant. In Table 8.3, the reference plant is a power plant of the same type as the power plant with CCS. Thus, the mitigation costs here represent the incremental cost of capturing and storing CO_2 from a particular type of plant.

In some situations, it can be useful to calculate a cost of CO_2 avoided based on a reference plant different from the CCS plant (e.g., PC or IGCC plant with CCS using an NGCC reference plant). In Table 8.4, the reference plant represents the least-cost plant that would "normally" be built at a particular location in the absence of a carbon constraint. In many regions today, this would be either a PC plant or an NGCC plant.

Table 8.4. Mitigation cost for different combinations of reference and CCS plants based on current technology and new power plants.

A CO_2 mitigation cost also can be defined for a collection of plants, such as a national energy system, subject to a given level of CO_2 abatement. In this case the plant-level product costs presented in this section would be used as the basic inputs to energy-economic models that are widely used for policy analysis and quantification of overall mitigation strategies and costs for CO_2 abatement. Section 8.3 discusses the nature of these models and presents illustrative model results, including the cost of CCS, its economic potential, and its relationship to other mitigation options.

8.3 CCS deployment scenarios

Energy-economic models seek the mathematical representation of key features of the energy system in order to represent the evolution of the system under alternative assumptions, such as population growth, economic development, technological change, and environmental sensitivity. These models have been employed increasingly to examine how CCS technologies would deploy in a greenhouse gas constrained environment. In this section we first provide a brief introduction to the types of energy and economic models and the main assumptions, which drive future greenhouse gas emissions and the corresponding measures to reduce them. Next we turn to the principal focus of this section, an examination of the literature based on studies using these energy and economic models, with an emphasis on what they say about the potential use of CCS technologies.

Box 8.2. Tonne carbon dioxide (tCO_2) vs. tonne carbon (tC) in energy-economic Models.

The convention in this report has been to report tCO_2 with the equivalent tC in parentheses. This convention was adopted because CCS technologies and their literature usually report CO_2. For example, a pipeline actually transports CO_2, not C equivalent. However, energy-economic modelling more often uses the units of C equivalent, as reflected in that literature. Therefore, in this section (8.3), which draws heavily from the energy-economy modelling community, we conform to their convention of reporting in tC. Because of the large quantity of numbers involved in both the text and figures, we will not put their equivalence in tCO_2. To convert, use the following formulas:

$tCO_2 = 3.67 * tC$ $US\$/tCO_2 = US\$/tC / 3.67$

8.3.1 Model approaches and baseline assumptions

The modelling of climate change abatement or mitigation scenarios is complex and a number of modelling techniques have been applied, including input-output models, macroeconomic (top down) models, computable general equilibrium (CGE) models and energy sector based engineering models (bottom-up).

8.3.1.1 Description of bottom-up and top down models

The component and systems level costs provided in Section 8.2 are based on technology-based bottom-up models. These models can range from technology-specific engineering-economic calculations embodied in a spreadsheet to broader multi-technology integrated partial equilibrium models. This may lead to two contrasting approaches, an engineering-economic one and a least-cost equilibrium one. In the first approach, each technology is assessed independently taking into account all its parameters; whereas partial equilibrium least-cost models consider all technologies simultaneously and at a higher level of aggregation and from this select the optimal mix of technologies in all sectors and for all time periods.

Top-down models evaluate the system from aggregate economic variables. Econometric relationships among aggregated variables are generally more reliable than those among disaggregated variables, and the behaviour of the models tends to be more stable. It is therefore common to adopt high levels of aggregation for top-down models; especially when they are applied to longer-term analyses. Technology diffusion is often described in these top-down models in a more stylized way, e.g., through aggregate production functions with price-demand or substitution elasticities.

Both types of models have their strengths and weaknesses. Top-down models are useful for among other things calculating gross economic cost estimates for emissions mitigation. Most of these top-down macro economic models tend to overstate costs of meeting climate change targets because, among other reasons, they neither sufficiently take account of the potential for no-regret measures nor are they particularly adept at estimating the benefits of climate change mitigation. On the other hand, many of these models - as well as bottom-up models - are not adept at representing economic and institutional inefficiencies, which would lead to an underestimation of emissions mitigation costs.

Technologically disaggregated bottom-up models can take some of these benefits into account but may understate the costs of overcoming economic barriers associated with their deployment in the marketplace. Recent modelling efforts have focused on the coupling of top-down and bottom-up models in order to develop scenarios that are consistent from both, the macroeconomic and systems engineering perspective. Readers interested in a more detailed discussion of these modelling frameworks and their application to understanding future energy, economic and emission scenarios are encouraged to consult the IPCC's Working Group III's assessment of the international work on both bottom-up and top-down analytical approaches contained in the TAR (Third assessment Report; IPCC, 2001).

8.3.1.2 Assumptions embodied in emissions baselines

Integrated Assessment Models (IAMs) are a particular type of energy and economic models and will be used here to describe the importance of emissions baselines before examining model

projections of potential future CCS use. IAMs integrate the simulation of climate change dynamics with the modelling of the energy and economic systems. A common and illuminating type of analyses conducted with IAM's and other energy and economic models is to calculate the cost differential or examine changes in the portfolio of energy technologies used between a baseline (i.e., no climate policy) scenario and a control scenario (i.e., a case where a specific set of measures designed to constrain GHG emissions is modelled). It is therefore important to understand what influences the character of these baseline scenarios. A number of parameters spanning economic, technological, natural resource, and demographic resources shape the energy use and resulting emissions trajectories of these baseline cases. How these parameters change with respect to time is also an important aspect that drives the baseline scenarios. A partial list of some of the major parameters that influence baseline scenarios includes items such as modelling assumptions centering on:

- Global and regional economic and demographic developments.
- Costs and availability of
  1) global and regional fossil fuel resources
  2) fossil-based energy conversion technologies (power generation, H_2 production, etc.), including technology specific parameters such as efficiencies, capacity factors, operation and maintenance costs as well as fuel costs.
  3) zero-carbon energy systems (renewables and nuclear), which might still be non-competitive in the baseline but may play a major role competing for market shares with CCS in the case that climate policies are introduced.
- Rates of technological change in the baseline and specific way in which technological change is parameterized.
- The relative contribution of CO_2 emissions from different economic sectors.

Modelling all of these parameters as well as alternative assumptions for them yields a large number of "possible futures", i.e., they yield a number of possible baseline scenarios. This is best exemplified by the work of the Special Report on Emission Scenarios (SRES, 2000) team which created four different narrative storylines and associated scenario families, and has identified six so-called "illustrative" scenario groups, labelled A1FI, A1B, A1T, A2, B1, B2, each representing different plausible combinations of socio-economic and technological developments in absence of any climate policy (for a detailed discussion of these cases see SRES, 2000). The six scenario groups depict alternative developments of the energy system, based on different assumptions on economic and demographic change, hydrocarbon resource availability, energy demand and prices, and technology costs and their performance. They lead to a wide range of possible future worlds and CO_2 emissions consistent with the full uncertainty range of the underlying literature (Morita and Lee, 1998). The cumulative emissions from 1990 to 2100 in the scenarios range from less than 2930 to 9170 $GtCO_2$ (800 to 2500 GtC). This range is divided into four intervals distinguishing between scenarios with high, medium-high, medium-low, and low emissions:

- High (≥6600 $GtCO_2$ or ≥1800 GtC)
- Medium-high (5320-6600 $GtCO_2$ or 1450-1800 GtC)
- Medium-low (4030-5320 $GtCO_2$ or 1100-1450 GtC)
- Low (≤4030 $GtCO_2$ or ≤1100 GtC)

As illustrated in Figure 8.3, each of the intervals contains multiple scenarios from more than one of the six SRES scenario groups (see the vertical bars on the right side of Figure 8.3, which show the ranges for cumulative emissions of the respective SRES scenario group). Other scenario studies, such as the earlier set of IPCC scenarios developed in 1992 (Pepper et al., 1992) project similar levels of cumulative emissions over the period 1990 to 2100 ranging from 2930 to 7850 $GtCO_2$ (800 to 2140 GtC). For the same time horizon, the IIASA-WEC scenarios (Nakicenovic et al., 1998)

report 2270-5870 $GtCO_2$ (620-1600 GtC), and the Morita and Lee (1998) database including more than 400 emissions scenarios report cumulative emissions up to 12280 $GtCO_2$ (3350 GtC).

Figure 8.3. Annual and cumulative global emissions from energy and industrial sources in the SRES scenarios ($GtCO_2$). Each interval contains alternative scenarios from the six SRES scenario groups that lead to comparable cumulative emissions. The vertical bars on the right-hand side indicate the ranges of cumulative emissions (1990-2100) of the six SRES scenario groups.

The SRES scenarios illustrate that similar future emissions can result from very different socio-economic developments, and that similar developments in driving forces can nonetheless result in widely different future emissions. The scenarios indicate also that the future development of energy systems will play a central role in determining future emissions and suggests that technological developments are at least as important a driving force as demographic change and economic development. These findings have major implications for CCS, indicating that the pace at which these technologies will be deployed in the future - and hence, also their long-term potential - is less affected by economic or demographic change, but rather by the choice of the technology path of the energy system, the major driver of future emissions. For a detailed estimation of the technical potential of CCS by sector for some selected SRES baseline scenarios, see Section 2.3.2. In the next section we shall discuss the economic potential of CCS in climate control scenarios.

8.3.2 CCS economic potential and implications

As shown by the SRES scenarios, uncertainties associated with alternative combinations of socio-economic and technological developments may lead to a wide range of possible future emissions. Each of the different baseline emissions scenarios has different implications for the potential use of CCS technologies in emissions control cases.[6] Generally, the size of the future market for CCS depends predominantly on the carbon intensity of the baseline scenario and the stringency of the assumed climate stabilization target. The higher the CO_2 emissions are in the baseline, the more emissions reductions are required to achieve a given level of allowable emissions, leading to larger markets for CCS. Likewise, the tighter the modelled CO_2 emissions constraint is the more CCS deployment there is likely to be. This section will examine what the literature says about possible CCS deployment rates, the timing of CCS deployment, the total deployment of these systems under various scenarios, the economic impact of CCS systems and how CCS systems interact with other emissions mitigation technologies.

8.3.2.1 Key drivers for the deployment of CCS

Energy and economic models are increasingly being employed to examine how CCS technologies would deploy in CO_2 emissions constrained environments (i.e., in control cases). A number of factors that drive the rate of CCS deployment and the scale of its ultimate deployment in modelled control cases have been identified:[7]

[6] As no climate policy is assumed in SRES, there is also no economic value associated with carbon. The potential for CCS in SRES is therefore limited to applications where the supplementary benefit of injecting CO_2 into the ground exceeds its costs (e.g., EOR or ECBM). The potential for these options is relatively small as compared to the long-term potential of CCS in stabilization scenarios. Virtually all global modelling exercises in the literature including SRES do not include these options, and hence, there is also no CCS system deployment assumed in the baseline scenarios.

[7] Integrated assessment models represent the world in an idealized way, employing different methodologies for the mathematical representation of socio-economic and technological developments in the real world. The representation of some real world factors, such as, institutional barriers, inefficient legal frameworks, transaction costs of carbon permit trading, potential free-rider behaviour of geopolitical agents, implications of public

1. *The policy regime*; the interaction between CCS deployment and the policy regime in which energy is produced and consumed cannot be overemphasized; the magnitude and timing of early deployment is strongly dependent on the policy environment; in particular the cumulative extent of deployment over the long term depends strongly on the stringency of the emissions mitigation regime being modelled; comparatively low stabilization targets (e.g., 450 ppmv) foster the relatively faster penetration of CCS and the more intensive use of CCS (where "intensity of use" is measured both in terms of the percentage of the emissions reduction burden shouldered by CCS as well as in terms of how many cumulative gigatons of CO_2 is to be stored) (Dooley, et al., 2004b, Gielen and Podanski, 2004, Riahi and Roehrl, 2000)
2. *The reference case (baseline)*; storage requirements for stabilizing CO_2 concentrations at a given level are very sensitive to the choice of the baseline scenario. That is, the assumed socio-economic and demographic trends, and particularly the assumed rate of technological change have a significant impact on CCS use (see Section 8.4.1, Riahi and Roehrl, 2000; Riahi *et al*., 2003);
3. *The nature, abundance and carbon intensity of the energy resources / fuels* assumed to exist in the future (e.g., a future world where coal is abundant and easily recoverable would use CCS technologies more intensively than a world in which natural gas or other less carbon intensive technologies are inexpensive and widely available), see Edmonds and Wise (1998) for a comparison of two alternative regimes of fossil fuel availability and their interaction with CCS; and Riahi and Roehrl (2000);
4. *The introduction of flexibility mechanisms such as emissions trading* can significantly influence the extent of CCS deployment. For example, an emissions regime with little or significantly constrained emissions trading between nations entails the use of CCS technologies sooner and more extensively than a world in which there is efficient global emissions trading and therefore lower carbon permit prices (e.g., Dooley *et al*., 2000 and Scott *et al*., 2004). Certain regulatory regimes that explicitly emphasize CCS usage can also accelerate its deployment (e.g., Edmonds and Wise 1998).
5. *The rate of technological change (induced through learning or other mechanisms)* assumed to take place with CCS and other salient mitigation technologies (e.g., Edmonds *et al*., 2003, or Riahi *et al*., 2003). For example, Riahi *et al.* (2003) indicate that the long-term economic potential of CCS systems would increase by a factor of 1.5 under the assumption that technological learning for CCS systems would take place at similar rates as observed historically for sulphur removal technologies when compared to the situation where no technological change is specified.[8]

The marginal value of CO_2 emission reduction permits is one of the most important mechanisms through which these factors impact CCS deployment. CCS systems tend to deploy quicker and more extensively in cases with higher marginal carbon values. Most energy and economic modelling done to date suggests that CCS systems begin to deploy at a significant level when carbon prices begin to reach approximately 25 - 30 US$/$tCO_2$ (90-110 US$/tC) (IEA, 2004; Johnson and Keith, 2004; Wise and Dooley, 2004; McFarland et al., 2004). The only caveat to this finding of the need for a value to carbon before these systems deploy is the "early opportunities" literature discussed below.

Before turning to a specific focus on the possible contribution of CCS in various emissions mitigation scenarios, it is worth reinforcing the point that there is a broad consensus in the technical

acceptance, has traditionally been a challenge in modelling. These factors are represented at various degrees (often generically) in these models.

[8] The factor increase of 1.5 corresponds to about 250 to 360 $GtCO_2$ of additional capture and storage over the course of the century.

literature that no single mitigation measure will be sufficient to achieve a stable concentration of CO_2. This means that the CO_2 emissions will most likely be reduced from baseline scenarios by a portfolio of technologies in addition to other social, behavioural and structural changes (Edmonds *et al*., 2003; Riahi and Roehrl, 2000). In addition, the choice of a particular stabilization level from any given baseline significantly affects the technologies needed for achieving the necessary emissions reduction (Edmonds *et al*., 2000; Roehrl and Riahi, 2000). For example, a wider range of technological measures and their widespread diffusion and more intensive use is required for stabilizing at 450 ppmv compared with stabilization at higher levels (Nakicenovic and Riahi, 2001). These and other studies (e.g., IPCC, 2001) have identified several classes of robust mitigation measures: demand reductions and/or efficiency improvements; substitution among fossil fuels; deployment of non-carbon energy sources (i.e., renewables and nuclear); CO_2 capture and storage; and afforestation and reforestation.

8.3.3 The share of CCS in total emissions mitigation

Integrated Assessment models attempt to capture the heterogeneity that characterizes energy demand, energy use and the varying states of development of energy technologies that are in use at any given point in time as well as across time in their modelling of energy and carbon markets. These Integrated Assessment tools are also used to model changes in market conditions that would shift the relative cost competitiveness of various energy technologies. For example, the choice of energy technologies would vary as carbon prices rise, as the population grows or as a stable population increases its standard of living. The graphs in Figure 8.4 portray how two different Integrated Assessment models (MiniCAM and MESSAGE) project the development of global primary energy (upper panels), the contribution of major mitigation measures (middle panels), and the marginal carbon permit price in response to a modelled policy that seeks to stabilize atmospheric concentrations of CO_2 at 550 ppmv consistent with the main greenhouse gas emissions drivers of the IPCC-SRES B2 scenario (see Box 8.3). As can be seen from Figure 8.4, CCS coupled with coal and natural gas fired electricity generation are key technologies in the mitigation portfolio in both scenarios and particularly in the later half of the century under this particular stabilization scenario. However, there is still a sizeable portion of the global demand for electricity being met by solar/wind, biomass, nuclear power, etc. Thus demonstrating that the world will continue to use a multiplicity of energy technologies to meet its energy demand and that across space and time a large portfolio of these technologies will be used at any one time.

Figure 8.4. The set of graphs portray how two different Integrated Assessment models (MiniCAM and MESSAGE) project the development of global primary energy (upper panels) and the corresponding contribution of major mitigation measures (middle panels). The lower panel depicts the marginal carbon permit price in response to a modelled mitigation regime that seeks to stabilize atmospheric concentrations of CO_2 at 550 ppmv. Both scenarios adopt harmonized assumptions with respect to the main greenhouse gas emissions drivers consistent with the IPCC-SRES B2 scenario. (Source: Dooley, et al., 2004b and Riahi and Roehrl 2000)

Box 8.3. Two illustrative 550 ppmv stabilization scenarios based on IPCC SRES B2.

The MESSAGE and MiniCAM scenarios illustrated in Figure 8.4 represent two alternative quantifications of the B2 scenario family of the IPCC SRES, used for subsequent CO_2 mitigation analysis exploring principal measures that would lead to the stabilization of atmospheric concentrations at 550 ppmv.

The scenarios are based on the B2 storyline, a narrative description of how the world evolves through the twenty-first century, and share harmonized assumptions concerning salient drivers of

CO_2 emissions, such as economic development, demographic change, and final energy demand. Consistent with the B2 storyline, gross world product is assumed to grow from US$ 20 trillion in 1990 to about US$ 235 trillion in 2100 in both scenarios, corresponding to a long-term average growth rate of 2.2%. Most of this growth takes place in today's developing countries. As to population development, the scenarios adopt the UN median 1998 population projection (UN, 1998), which depicts a continuation of historical trends, including recent faster-than-expected fertility declines, toward a completion of the demographic transition within the next century. Global population increases to about 10 billion by 2100. Final energy intensity of the economy declines at about the long-run historical rate of about one percent per year through 2100. On aggregate these trends constitute "dynamics-as-usual" developments, corresponding to middle of the road assumptions compared to the scenario uncertainty range from the literature (Morita and Lee, 1999).

Besides the above mentioned similarities, the MiniCAM and MESSAGE scenarios rely on alternative interpretations of the B2 storyline concerning a number of other important assumptions that affect the potential future deployment of CCS, such as, fossil resource availability, long-term potentials for renewable energy, development of fuel prices, structure of the energy system and sectoral breakdown of energy demand, technology costs, and in particular technological change (future prospects for costs and performance improvements for specific technologies and technology clusters).

Thus, the two scenarios portray alternative but internally consistent developments of the energy technology portfolio, associated CO_2 emissions, as well as the deployment of CCS and other mitigation technologies as response to the 550 ppmv CO_2 stabilization target, adopting the same assumptions for economic, population, and aggregated demand growth. The comparison of the scenario's portfolio of mitigation options (Figure 8.4) illustrates the importance of CCS as part of the mitigation portfolio. For more details see Dooley et al., 2004b and Riahi and Roehrl, 2000.

When modelling how various technologies will contribute to the goal of addressing climate change, these technologies are modelled in such a way that they are all competing for market share to provide the energy services and emissions reduction required by society as this is what would happen in reality. The potential and costs of these options are subject to large uncertainties, and therefore the absolute deployment of CCS depends on various scenario-specific assumptions consistent with the underlying storyline and the way they are interpreted in the different models. In light of this competition and the wide variety of possible emissions futures, the contribution of CCS in total emissions reduction can only be assessed within relatively wide margins.

The uncertainty with respect to the future deployment of CCS and its contribution to total emissions reductions for achieving stabilization of CO_2 concentrations between 450 and 750 ppmv is illustrated by the IPCC TAR mitigation scenarios (Morita *et al*., 2000; 2001). The TAR mitigation scenarios are based upon SRES baseline scenarios and were developed by nine different modelling teams. In total, 76 mitigation scenarios were developed for TAR, and about half of them (36 scenarios from three alternative models: DNE21, MARIA, and MESSAGE) consider CO_2 capture and storage explicitly as a mitigation option. An overview of the TAR scenarios is presented in Morita *et al.* (2000), comprising eleven publications from individual modelling teams on their scenario assumptions and results.

As illustrated in Figure 8.5, which is based upon the TAR mitigation scenarios, the average share of CCS in total emissions reductions may range between 15% for scenarios aiming at the stabilization

of CO_2 concentrations at 750 ppmv to 54% for 450 ppmv scenarios.[9] The full uncertainty spanned by the set of TAR mitigation scenarios, though, includes extremes on the high as well as the low side, ranging from scenarios with zero CCS contributions to scenarios with CCS shares of more than 90 percent in total emissions abatement.

Figure 8.5. Relationship between (1) the imputed share of CCS in total cumulative emissions reductions in percent and (2) total cumulative CCS deployment in $GtCO_2$ (2000-2100). The scatter plots depict values for individual TAR mitigation scenarios for the six SRES scenario groups. Vertical dashed lines show the average share of CCS in total emissions mitigation across the 450 to 750 ppmv stabilization scenarios, and the dashed horizontal lines illustrate the scenario's average cumulative storage requirements across 450 to 750 ppmv stabilization.

8.3.3.1 Cumulative CCS deployment

Top-down and bottom-up energy-economic models have been used to examine the likely total deployment of CCS technologies (expressed in GtC). These analyses reflect that the future usage of CCS technologies is associated with large uncertainties. As illustrated by the IPCC-TAR mitigation scenarios, global cumulative CCS during the 21st century could range - depending on the future characteristics of the reference world (i.e., baselines) and the employed stabilization target (450 to 750 ppmv) - from zero to more than 5500 $GtCO_2$ (1500 GtC) (see Figure 8.6). The average cumulative CO_2 storage (2000-2100) across the six scenario groups shown in Figure 8.6 ranges from 380 $GtCO_2$ (103 GtC) in the 750 ppmv stabilization scenarios up to 2160 $GtCO_2$ (590 GtC) in the 450 ppmv scenarios (Table 8.5).[10] However, it is important to note that the majority of the six individual TAR scenarios (from the 20th to the 80th percentile) tend to cluster in the range of 220-2200 $GtCO_2$ (60-600 GtC) for the four stabilization targets (450 - 750 ppmv).

Figure 8.6. Global cumulative CO_2 storage (2000-2100) in the IPCC TAR mitigation scenarios for the six SRES scenario groups and CO_2 stabilization levels between 450 and 750 ppmv. Values refer to averages across scenario results from different modelling teams. The contribution of CCS increases with the stringency of the stabilization target and differs considerably across the SRES scenario groups.

The deployment of CCS in the TAR mitigation scenarios is comparable to results from similar scenarios studies projecting storage requirements of 576-1370 $GtCO_2$ (157-374 GtC) for stabilization scenarios that span 450 to 750 ppmv (Edmonds *et al*., 2000) and 370 to 1250 $GtCO_2$ (100 to 340 GtC) for stabilization scenarios that span 450 to 650 ppmv (Dooley and Wise, 2003). Riahi *et al*. (2003) projects 330-890 $GtCO_2$ (90-243 GtC) of stored CO_2 over the course of the current century for various 550 ppmv stabilization cases. Fujii and Yamaji (1998) have also included ocean storage as an option. They calculate that for a stabilization level of 550 ppmv, 920 $GtCO_2$ (250 GtC) of the emissions reductions could be provided by the use of CCS technologies and that approximately 1/3 of this could be stored in the ocean. This demand for CO_2 storage appears to be within global estimates of total CO_2 storage capacity presented in Chapters 5 and 6.

[9] The range for CCS mitigation in the TAR mitigation scenarios is calculated based upon the cumulative emissions reductions from 1990 to 2100, and represents the average contribution for 450 and 750 ppmv scenarios across alternative modelling frameworks and SRES baseline scenarios. The full range across all scenarios for 450 ppmv is 20 to 95% and 0 to 68% for 750 ppmv scenarios respectively.

[10] Note that Table 8.5 and Figure 8.6 depict average values of CCS across alternative modelling frameworks used for the development of the TAR mitigation scenarios. The deployment of CCS over time as well as cumulative CO_2 storage of individual TAR mitigation scenarios are illustrated in Figures 8.5 and 8.7.

8.3.3.2 Timing and deployment rate

Recently, two detailed studies of the cost of CO_2 transport and storage costs have been completed for North America (Dooley et. al. 2004a) and Western Europe (Wildenborg et. al., 2004). These studies concur about the large potential of CO_2 storage capacity in both regions. Well over 80% of the emissions from current CO_2 point sources could be transported and stored in candidate geologic formations for less than 12-15 US$/t$CO_2$ in North America and 25 US$/t CO_2 in Western Europe. These studies are the first to define at a continental scale a "CO_2 storage supply curve", conducting a spatially detailed analysis in order to explore the relationship between the price of CO_2 transport and storage and the cumulative amount of CO_2 stored. Both studies conclude that at least for these two regions the CO_2 storage supply curves are dominated by a very large single plateau (hundreds to thousands of gigatonnes of CO_2) in which costs are roughly constant[11]. In other words, at a practical level the cost of CO_2 transport and storage in these regions will have a cap. These studies as well as a handful of others (see for example IEA GHG, 2002) have also shown that whether there are early (i.e., low cost) opportunities for capture and storage of CO_2 hinges upon a number of factors: an inexpensive (and therefore most likely high purity) source of CO_2, an (potentially) active area of advanced hydrocarbon recovery (either EOR or ECBM), and the CO_2 point source and the candidate storage reservoir being in relative close proximity to minimize transportation costs. These bottom-up studies provide some of the most detailed insights into the graded CCS resources presently available, showing that the set of CCS opportunities likely to be encountered in the real world will be very heterogeneous. These studies as well as those based upon more top-down modelling approaches also indicate that once the full cost of the complete CCS system are accounted for, CCS systems are unlikely to deploy on a large scale in the absence of an explicit policy or regulatory regime that substantially limits greenhouse gas emissions to the atmosphere. The literature and current industrial experience indicates that in the absence of measures to limit CO_2 emissions there are only small, niche opportunities for CCS technologies to deploy. These early opportunities for CCS deployment could provide experience with CCS deployment including creating parts of the infrastructure and knowledge base needed for future large-scale deployment of CCS systems.

Most analyses of least cost CO_2 stabilization scenarios indicate that while there is significant penetration of CCS systems over the next decades, the majority of CCS deployment will occur in the second half of this century (Edmonds *et al*. (2000, 2003); Edmonds and Wise (1998); Riahi *et al*. (2003)). A primary reason for this trend is that generally the stabilization of CO_2 concentrations at relatively low levels (<650 ppmv) leads to progressively more constraining mitigation regimes over time resulting in carbon permit prices that start out quite low and steadily rise over the course of this century. The TAR mitigation scenarios (Morita *et al*., 2000) based upon the SRES baselines report cumulative CO_2 storage due to CCS ranging between zero to 1100 $GtCO_2$ (300 GtC) for the first half of the century, with the majority of the scenarios clustering below 185 $GtCO_2$ (50 GtC). In comparison, the cumulative contributions of CCS range from zero to 4770 $GtCO_2$ (1300 GtC) in the second half of the century, with the majority of the scenarios lying below 1470 $GtCO_2$ (400 GtC). The deployment of CCS over time in the TAR mitigation scenarios is illustrated in Figure 8.7. As can be seen, the use of CCS is highly dependent upon the underling base case. For example in the high economic growth and carbon-intensive baseline scenarios (A1FI), the development path of CCS is characterized by steadily increasing contributions, driven by the rapidly growing use of hydrocarbon resources. In contrast, other scenarios (e.g., A1B and B2) depict CCS deployment to peak during the second half of the century. In a number of these scenarios, the contribution of CCS declines to less than 11 $GtCO_2$ /yr (3 GtC /yr) until the end of the century. These reflect that CCS

[11] See Chapter 5 for a full assessment of the estimates of geological storage capacity.

could be viewed as a transitional mitigation option (bridging the transition from today's fossil-intensive energy system to a post-fossil system with sizable contributions from renewables).

Figure 8.7. Deployment of CCS systems as a function of time from 1990 to 2100 in the IPCC TAR mitigation scenarios aiming at the stabilization of atmospheric CO_2 concentrations between 450 to 750 ppmv. Coloured thick lines show the minimum and maximum contribution of CCS for each SRES scenario group, and thin lines depict the contribution of individual scenarios. Vertical axes on the right hand side illustrate the range of CCS deployment across the stabilization levels for each SRES scenario group in the year 2100.

Using these models' relatively coarse top-down view of the world, there is less agreement as to when the first commercial CCS units will become operational. This is at least in part because of the importance of policy in creating the context in which initial units will deploy. For example, McFarland *et al*. (2003) foresee CCS deployment beginning around 2035. Other modelling exercises have shown CCS systems begin - at a lower level of less than 370 $MtCO_2$ /yr (100 MtC/yr) - to deploy in the period 2005-2020 (see for example Dooley *et al*., 2000) and in an examination of CCS deployment in Japan, Akimoto *et al*. (2003) show CCS deployment beginning in 2010-2020. In a large body of literature (Edmonds *et al*. 2003; Dooley and Wise, 2003; Riahi *et al*. 2003; IEA, 2004), there is agreement that in a CO_2-constrained world CCS systems might begin to deploy in the next few decades and that this deployment would expand significantly after the middle of the century. The differing estimates as to when CCS systems deploy is attributable to the varied ways that energy and economic models parameterise CCS systems and to which extent the potential for early opportunities such as for EOR or ECBM is taken into account. Other factors that influence the timing of the CCS diffusion are the rate of increase and absolute level of the models' carbon price.

8.3.3.3 Geographic distribution

McFarland *et al*. (2003) foresee eventual deployment of CCS technologies throughout the world but note that the timing of the entry of CCS technologies into a particular region is influenced by local conditions such as the relative price of coal and natural gas in a region. Dooley *et al*. (2002) show that the policy regime, and in particular the extent of emissions trading can influence where CCS technologies are deployed. In the specific case examined by this paper, it was demonstrated that in cases where emissions trading was severely constrained (and therefore the cost of abatement was higher), CCS technologies tended to deploy more quickly and more extensively in the US and the EU. On the other hand when there was an efficient emissions trading system that spanned all of the Annex B nations, CCS was used less intensively and CCS utilization was spread more evenly across these nations as the EU and US find it cheaper to buy CCS-derived emission allowances from regions like the Former Soviet Union.

Table 8.5 gives the corresponding deployment of CCS in the IPCC TAR mitigation scenarios for four world-regions.[12] All values are given as averages across scenario results from different modelling teams and the data in this table help to demonstrate a common and consistent theme across the literature that over the course of this century CCS will deploy throughout the world with the largest deployment being in the developing nations of today as these will be tomorrow's largest

[12] The OECD90 region includes the countries belonging to the OECD in 1990. The REF ("reforming economies") region aggregates the countries of the Former Soviet Union and Eastern Europe. The ASIA region represents the developing countries on the Asian continent. The ROW region covers the rest of the world, aggregating countries in sub-Saharan Africa, Latin America and the Middle East. For more details see SRES, 2000.

emitters of CO_2 and therefore be likely candidates for adopting CCS to control their growing emissions.[13]

Table 8.5 Cumulative CO_2 storage (2000 to 2100) in the IPCC TAR mitigation scenarios in $GtCO_2$. CCS contributions for the world and for the four SRES regions are shown for four alternative stabilization targets (450, 550, 650, and 750 ppmv) and six SRES scenario groups. Values refer to averages across scenario results from different modelling teams

Fujii et al. (2002) note that the actual deployment of CCS technologies in any given region will depend upon a host of geological and geographical conditions that are presently poorly represented in top down energy and economic models. In an attempt to address the shortcomings noted by Fujii et. al (2002) and others especially as it applies to the way in which the cost of CO_2 transport and storage are parameterized in top-down models, Dooley et al. (2004b) have employed graded CO_2 storage supply curves for all regions of the world based upon a preliminary assessment of the literature's estimate of regional CO_2 storage capacity. In this framework where the cost of CO_2 storage varies across the globe depending upon the quantity, quality (including proximity) and type of CO_2 storage reservoirs present in the region as well as the demand for CO_2 storage (driven by factors such as the size of the regional economy, the stringency of the modelled emissions reduction regime), the authors show that the use of CCS across the globe can be grouped into three broad categories: (1) countries in which the use of CCS does not appear to face either an economic or physical constraint on CCS deployment given the large potential CO_2 storage resource in comparison to projected demand (e.g., Australia, Canada, and the United States) and therefore CCS should deploy to the extent that it makes economic sense to do so; (2) countries in which the supply of potential geological storage reservoirs (the authors did not consider ocean storage) is small in comparison to potential demand (e.g., Japan and South Korea) and therefore other abatement options must be pressed into service to meet the modelled emissions reduction levels; and (3) the rest of the world in which the degree to which CCS deployment is constrained is contingent upon the stringency of the emission constraint and the useable CO_2 storage resource. The authors note that discovering the true CO_2 storage potential in regions of the world is a pressing issue as knowing whether a country or a region has "sufficient" CO_2 storage capacity is a critical variable in these modelling analyses as it can fundamentally alter the way in which a country's energy infrastructure evolves in response to various modelled emissions constraints.

8.3.3.4 Long term economic impact

An increasing body of literature has been analyzing short- and long-term financial requirements for CCS. The World Energy Investment Outlook 2003 (IEA, 2003) estimates an upper bound for investment in CCS technologies for the OECD of about US$ 350 to US$ 440 billion over the next 30 years, assuming that all new power plant installations would be equipped with CCS. Similarly, Riahi *et al.* (2004) estimate that upfront investments for initial niche market applications and demonstration plants could amount to about US$ 70 billion or 0.2 percent of the total global energy systems costs over the next 20 years. This would correspond to a market share of CCS of about 3.5 % of total installed fossil power generation capacities in the OECD countries by 2020, where most of the initial CCS capacities are expected to be installed.

Long-term investment requirements for the full integration of CCS in the electricity sector globally are subject to large uncertainties. Analyses with integrated assessment models indicate that the

[13] This trend is particularly illustrated by the most left-hand column of Table 8.5, which gives the average CCS deployment across all scenarios from the various models. Note, nevertheless, a few scenarios belonging to the B1 and B2 scenario family, which depict larger deployment of CCS in the developed world.

costs of decarbonizing the electricity sector via CCS might be about three to four percent of total energy-related systems costs over the course of the century (Riahi et al., 2004). Most importantly, these models do also point out that the opportunity costs of CCS not being part of the CO_2 mitigation portfolio would be significant. Edmonds *et al*. (2000) indicate that savings over the course of this century associated with the wide-scale deployment of CCS technologies when compared to a scenario in which these technologies do not exist could be in the range of tens of billions of 1990 U.S. dollars for high CO_2 concentrations limits such as 750 ppm to trillions of dollars for more stringent CO_2 concentrations such as 450 ppm.[14] Dooley *et al*. (2002) estimate cost savings in excess of 36% and McFarland et al. (2004) a reduction in the carbon permit price by 110 US$/tCO_2$ in scenarios where CCS technologies are allowed to deploy when compared to scenarios in which CCS technologies are not allowed to deploy.

8.3.3.5 Interaction with other technologies

As noted above the future deployment of CCS will depend on a number of factors, many of which interact with each other. The deployment of CCS will be impacted by factors such as the development and deployment of renewable energy and nuclear power (Mori, 2000). Edmonds *et al*. (2003) reports that CCS technologies can synergistically interact with other technologies and in doing so help to lower the cost and therefore increase the overall economic potential of less carbon-intensive technologies involved. Edmonds *et al*. (2003) note that these synergies are perhaps particularly important for the combination of CCS, H_2 production technologies and H_2 end-use systems (e.g., fuel cells). On the other hand, the widespread availability of CCS technologies imply an ability to meet a given emissions reduction at a lower marginal cost, which decreases the demand for substitute technologies at the margin, i.e. CCS is competing with some technologies, such as energy intensity improvements, nuclear, fusion, solar power options, and wind. The nature of that interaction depends strongly on the climate policy environment and the costs and potential of alternative mitigation options, which are subject to large variations depending on site-specific, local conditions (IPCC, 2001). On the spatially more aggregated global level, this variation translates into the parallel deployment of alternative options, noting the importance of a diversified technology portfolio in addressing emissions mitigation in a cost-effective way.

An increasing body of literature (Willams, 1998, Obersteiner *et al*., 2002; Rhodes and Keith, 2003; Makihira *et al*., 2003; Edmonds *et al*., 2003, Möllersten et al., 2003) has begun to examine the use of CCS systems with biomass-fed energy systems to create useful energy (electricity or transportation fuels) as well as excess emissions credits via the system's resulting "negative emissions". These systems can be fuelled solely by biomass, or biomass can be co-fired in conventional coal-burning plants, in which case the quantity is normally limited to about 10-15% of the energy input. Obersteiner et al. (2002) performed an analysis based on the SRES scenarios, estimating that 880 to 1650 $GtCO_2$ (240 to 450 GtC) of the scenario's cumulative emissions that are vented during biomass-based energy-conversion processes could potentially be available for capture and storage over the course of the century. Rhodes and Keith (2003) note that while this coupled bio-energy CCS system would generate expensive electricity in a world of low carbon prices, in a world where carbon prices were in excess of 54.5 US$/tCO_2$ (200 US$/tC) this system could produce competitively priced electricity. Similarly, Makihira *et al*. (2003) estimate that CO_2 capture during hydrogen production from biomass could become competitive at carbon prices above 54.5 to 109 US$/tCO_2$ (200 to 400 US$/tC).

[14] Savings are measured as imputed gains of GDP due CCS deployment, in contrast to a world where CCS is not considered to be part of the mitigation portfolio.

8.4 Economic impacts of different storage times

As discussed in their respective chapters, geological and ocean storage might not provide for permanent storage of all of the CO_2 injected. The question arises about how the possibility of leakage from reservoirs can be taken into account in the evaluation of different storage options and in the comparison of CO_2 storage with mitigation options avoiding CO_2 emissions.

Chapters 5 and 6 discuss the expected fractions of CO_2 retained in storage for geological and ocean reservoirs, respectively. For example, Box 6.7 suggests four types of measures for ocean storage: storage efficiency, airborne fraction, net present value, and global warming potential. In Chapter 9, there is a discussion of accounting issues related to the possible impermanence of stored CO_2. Chapter 9 also contains a review of the broader literature related to the value of delayed emissions, primarily focused on sequestration in the terrestrial biosphere. In this section, we focus specifically on the economic impacts of differing storage times as it relates to geological and ocean reservoirs.

Herzog *et al*. (2003) suggest that CO_2 storage and leakage can be looked upon as two separate, discrete events. They represent the value of temporary storage as a familiar economic problem, with explicitly stated assumptions about the discount rate and carbon prices. If someone stores a tonne of CO_2 today, they will be credited with today's carbon price. Any future leakage will have to be compensated by paying the carbon price in effect at that time. Whether non-permanent storage options will be economically attractive depends on assumptions about the leakage rate, discount rate and relative carbon permit prices. In practice this may turn out to be difficult since the commercial entity that undertakes the storage may no longer exist when leakage rates have been clarified (as Baer (2003) points out), and hence governments or society at large might need to cover the leakage risk of many storage sites rather than the entity that undertakes the storage.

Ha-Duong and Keith (2003) explore the trade-offs between discounting, leakage, the cost of CO_2 storage and the energy penalty. They use both an analytical approach and an integrated assessment numerical model in their assessment. In the latter case with CCS modelled as a backstop technology, they find that for an optimal mix of CO_2 abatement and CCS technologies "a (annual) leakage rate of 0.1% is nearly the same as perfect storage while a leakage rate of 0.5% renders storage unattractive".

Some fundamental points about the limitations of the economic valuation approaches presented in the literature have been raised by Baer (2003). He argues that financial efficiency, which is at the heart of the economic approaches to the valuation of and the decision on non-permanent storage is only one of a number of important criteria to be considered. Baer points out that at least three risk categories should to be taken into account as well:

- Ecological risk - the possibility that 'optimal' leakage may preclude future climate stabilization
- Financial risk - the possibility that future conditions will cause carbon prices to greatly exceed current expectations, with consequences for the maintenance of liability and distribution of costs; and
- Political risk - the possibility that institutions with an interest in CO_2 storage may manipulate the regulatory environment in their favour.

As these points have not been extensively discussed in the literature so far, the further development of the scientific debate on these issues remains to be seen.

In summary, within this purely economic framework, the few studies that have looked at this topic indicate that some CO_2 leakage can be accommodated while still making progress towards the goal

of stabilizing atmospheric concentrations of CO_2. However, due to the uncertainties of the assumptions, the impact of different leakage rates, and hence the impact of different storage times, is hard to quantify.

8.5 Gaps in knowledge

Cost developments for CCS technologies are now estimated based on literature, expert views and a few recent CCS deployments. Costs of large-scale integrated CCS applications are still uncertain and their variability depends among others on many site-specific conditions. Especially for large-scale CCS biomass based applications, there is a lack of experience and therefore little information in the literature about the costs of these systems.

Little empirical evidence exists about possible cost decreases related to "learning by doing" for integrated CCS systems since the demonstration and commercial deployment of these systems has only recently begun. Furthermore, the impact of targeted research, development and deployment CCS investments (RD&D) on the level and rate of CCS deployment is poorly understood at this time. This lack in knowledge about how technologies will deploy in the future and the impact of RD&D on the technology's deployment is a generic issue and is not is not specific to CCS deployment.

In addition to current and future CCS technological costs, there are other possible issues that are not well known at this point which would impact the future deployment of CCS systems e.g., costs related to the monitoring and regulatory framework, possible environmental damage costs, costs associated with liability and possible public acceptance issues.

Full life cycle costs assessments for deployed CCS systems -- and in particular the economic impact of the capture, transport and storage of non-pure CO_2 streams -- are not known at this moment.

The development of bottom up CCS deployment cost curves – taking into account the interplay between large CO_2 point sources and available storage capacity in various regions of the world should continue as these cost curves would help to illuminate how CCS technologies will deploy in practice and would also help improve the economic modelling of CCS deployment in response to various modelled scenarios.

Recent changes in energy prices and changes in policy regimes related to climate change are not fully reflected in the literature that existed at the time of writing of this Chapter. This suggests a need for a continuous effort to update analyses and perhaps perform a range of scenarios with a wider range of assumptions (e.g., fuel prices, climate policies) in order to understand better the robustness and sensitivity of the current outcomes.

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Tables

Table 8.1. Summary of new plant performance and CO_2 capture cost based on current technology.

Performance and Cost Measures	New NGCC Plant			New PC Plant			New IGCC Plant			New Hydrogen Plant			(Units for H_2 Plant)
	Range		Rep.	Range		Rep.	Range		Rep.	Range		Rep.	
	low	high	Value	low	high	Value	low	high	Value	low	high	Value	
Emission rate w/o capture (kg CO_2/MWh)	344 - 379		*367*	736 - 811		*762*	682 - 846		*773*	78 - 174		*137*	kg CO_2/GJ (w/o capture)
Emission rate with capture (kg CO_2/MWh)	40 - 66		*52*	92 - 145		*112*	65 - 152		*108*	7 - 28		*17*	kg CO_2/GJ (with capture)
Percent CO_2 reduction per kWh (%)	83 - 88		*86*	81 - 88		*85*	81 - 91		*86*	72 - 96		*86*	% reduction/unit of product
Plant efficiency w/ capture, LHV basis (%)	47 - 50		*48*	30 - 35		*33*	31 - 40		*35*	52 - 68		*60*	Capture plant efficiency (% LHV)
Capture energy reqm't. (% more input/MWh)	11 - 22		*16*	24 - 40		*31*	14 - 25		*19*	4 - 22		*8*	% more energy input/GJ product
Total capital reqm't. w/o capture (US$/kW)	515 - 724		*568*	1161 - 1486		*1286*	1169 - 1565		*1326*	*[No unique normalization for multi-product plants]*			Capital reqm't. w/o capture
Total capital reqm't. with capture (US$/kW)	909 - 1261		*998*	1894 - 2578		*2096*	1414 - 2270		*1825*				Capital reqm't. with capture
Percent increase in capital cost w/ capture (%)	64 - 100		*76*	44 - 74		*63*	19 - 66		*37*	-2 - 54		*18*	% increase in capital cost
COE w/o capture (US$/MWh)	31 - 50		*37*	43 - 52		*46*	41 - 61		*47*	6.5 - 10.0		*7.8*	H_2 cost w/o capture (US$/GJ)
COE with capture only (US$/MWh)	43 - 72		*54*	62 - 86		*73*	54 - 79		*62*	7.5 - 13.3		*9.1*	H_2 cost w/ capture (US$/GJ)
Increase in COE w/ capture (US$/MWh)	12 - 24		*17*	18 - 34		*27*	9 - 22		*16*	0.3 - 3.3		*1.3*	Increase in H_2 cost (US$/GJ)
Percent increase in COE w/ capture (%)	37 - 69		*46*	42 - 66		*57*	20 - 55		*33*	5 - 33		*15*	% increase in H_2 cost
Cost of CO_2 captured (US$/t$CO_2$)	33 - 57		*44*	23 - 35		*29*	11 - 32		*20*	2 - 39		*12*	US$/t$CO_2$ captured
Cost of CO_2 avoided (US$/t$CO_2$)	37 - 74		*53*	29 - 51		*41*	13 - 37		*23*	2 - 56		*15*	US$/t$CO_2$ avoided
Capture Cost Confidence Level (see Table 3.7)	moderate			moderate			moderate			moderate to high			Confidence Level (see Table 3.7)

Notes: [a] Ranges and representative values are based on data from Tables 3.7, 3.9, 3.10 and 3.11. All costs in this table are for capture only and do not include the costs of CO_2 transport and storage; see Chapter 8 for total CCS costs. [b] All PC and IGCC data are for bituminous coals only at costs of 1.0-1.5 US$/GJ (LHV); all PC plants are supercritical units. [c] NGCC data based on natural gas prices of 2.8-4.4 US$/GJ (LHV basis). [d] Costs are in constant US$ (approx. year 2002 basis). [e] Power plant sizes range from approximately 400-800 MW without capture and 300-700 MW with capture. [f] Capacity factors vary from 65-85% for coal plants and 50-95% for gas plants (average for each=80%). [g] Hydrogen plant feedstocks are natural gas (4.7-5.3 US$/GJ) or coal (0.9-1.3 US$/GJ); some plants in dataset produce electricity in addition to hydrogen. [h] Fixed charge factors vary from 11-16% for power plants and 13-20% for hydrogen plants. [i] All costs include CO_2 compression but not additional CO_2 transport and storage costs.

Table 8.2. Estimates of CO_2 storage costs.

Option	Representative Cost Range (US$/tonne CO_2 stored)	Representative Cost Range (US$/tonne C stored)
Geological - Storage[1]	0.5-8.0	2-29
Geological - Monitoring	0.1-0.3	0.4-1.1
Ocean[2]		
Pipeline	6-31	22-114
Ship (Platform or Moving Ship Injection)	12-16	44-59
Mineral Carbonation[3]	50-100	180-370

[1] Does not include monitoring costs.
[2] Includes offshore transportation costs; range represents 100-500 km distance offshore and 3000 m depth.
[3] Unlike geological and ocean storage, mineral carbonation requires significant energy inputs equivalent to approximately 40% of the power plant output.

Table 8.3a. Range of total costs for CO_2 capture, transport, and geological storage based on current technology for new power plants.

	Pulverized Coal Power Plant	Natural Gas Combined Cycle Power Plant	Integrated Coal Gasification Combined Cycle Power Plant
Cost of Electricity without CCS (US$/MWh)	43-52	31-50	41-61
Power Plant with Capture			
Increased Fuel Requirement (%)	24-40	11-22	14-25
CO_2 Captured (kg/MWh)	820-970	360-410	670-940
CO_2 Avoided (kg/MWh)	620-700	300-320	590-730
% CO_2 Avoided	81-88	83-88	81-91
Power Plant with Capture and Geological Storage[15]			
Cost of Electricity (US$/MWh)	63-99	43-77	55-91
Electricity Cost increase (US$/MWh)	19-47	12-29	10-32
% increase	43-91	37-85	21-78
Mitigation Cost (US$/t$CO_2$ avoided)	30-71	38-91	14-53
Mitigation Cost (US$/tC avoided)	110-260	140-330	51-200
Power Plant with Capture and Enhanced Oil Recovery[16]			
Cost of Electricity (US$/MWh)	49-81	37-70	40-75
Electricity Cost increase (US$/MWh)	5-29	6-22	(-5)-19
% increase	12-57	19-63	(-10)-46
Mitigation Cost (US$/t$CO_2$ avoided)	9-44	19-68	(-7)-31
Mitigation Cost (US$/tC avoided)	31-160	71-250	(-25)-120

[15] Capture costs represent range from Tables 3.7, 3.9 and 3.10. Transport costs range from \$0-5/tCO_2. Geological storage cost (including monitoring) range from 0.6-8.3 US$/t$CO_2$.
[16] Capture costs represent range from Tables 3.7, 3.9 and 3.10. Transport costs range from 0-5 US$/t$CO_2$ stored Costs for geological storage including EOR range from -10 to -16 US$/t$CO_2$.stored

Table 8.3b. Range of total costs for CO_2 capture, transport, and geological storage based on current technology for a new hydrogen production plant.

	Hydrogen Production Plant
Cost of H_2 without CCS (US$/GJ)	6.5-10.0
Hydrogen Plant with Capture	
Increased Fuel Requirement (%)	4-22
CO_2 Captured (kg/GJ)	75-160
CO_2 Avoided (kg/GJ)	60-150
% CO_2 Avoided	73-96
Hydrogen Plant with Capture and Geological Storage[17]	
Cost of H_2 (US$/GJ)	7.6-14.4
H_2 cost increase (US$/GJ)	0.4-4.4
% increase	6-54
Mitigation Cost (US$/t$CO_2$ avoided)	3-75
Mitigation Cost (US$/tC avoided)	10-280
Hydrogen Plant with Capture and Enhanced Oil Recovery[18]	
Cost of H_2 (US$/GJ)	5.2-12.9
H_2 cost increase (US$/GJ)	(-2.0)-2.8
% increase	(-28)-28
Mitigation Cost (US$/t$CO_2$ avoided)	(-14)-49
Mitigation Cost (US$/tC avoided)	(-53)-180

Table 8.4. Mitigation cost for different combinations of reference and CCS plants based on current technology and new power plants.

	NGCC Reference Plant		**PC Reference Plant**	
	$/t$CO_2$ avoided	**$/tC avoided**	**$/t$CO_2$ avoided**	**$/tC avoided**
Power Plant with Capture and Geological Storage				
NGCC	40 – 90	140 – 330	20 – 60	80 – 220
PC	70 – 270	260 – 980	30 – 70	110 – 260
IGCC	40 – 220	150 – 790	20 – 70	80 – 260
Power Plant with Capture and EOR				
NGCC	20 – 70	70 – 250	1 – 30	4 – 130
PC	50 – 240	180 – 890	10 – 40	30 – 160
IGCC	20 – 190	80 – 710	1 – 40	4 – 160

[17] Capture costs represent range from Table 3.11. Transport costs range from $0-5/t$CO_2$. Geological storage cost (including monitoring) range from 0.6-8.3 US$/t$CO_2$.

[18] Capture costs represent range from Table 3.11. Transport costs range from 0-5 US$/t$CO_2$. EOR credits range from 10-16 US$/t$CO_2$.

Table 8.5. Cumulative CO_2 storage (2000 to 2100) in the IPCC TAR mitigation scenarios in $GtCO_2$. CCS contributions for the world and for the four SRES regions are shown for four alternative stabilization targets (450, 550, 650, and 750 ppmv and six SRES scenario groups). Values refer to averages across scenario results from different modelling teams.

	All scenarios (average)	A1			A2	B2	B1
		A1FI	A1B	A1T			
WORLD							
450 ppmv	2162	5628	2614	1003	1298	1512	918
550 ppmv	898	3462	740	225	505	324	133
650 ppmv	614	2709	430	99	299	149	0
750 ppmv	377	1986	0	0	277	0	0
OECD90*							
450 ppmv	551	1060	637	270	256	603	483
550 ppmv	242	800	202	82	174	115	80
650 ppmv	172	654	166	54	103	55	0
750 ppmv	100	497	0	0	104	0	0
REF*							
450 ppmv	319	536	257	152	512	345	110
550 ppmv	87	233	99	42	55	79	16
650 ppmv	55	208	56	0	31	37	0
750 ppmv	36	187	0	0	28	0	0
ASIA*							
450 ppmv	638	2207	765	292	156	264	146
550 ppmv	296	1262	226	47	153	67	20
650 ppmv	223	1056	162	20	67	33	0
750 ppmv	111	609	0	0	57	0	0
ROW*							
450 ppmv	652	1825	955	289	366	300	179
550 ppmv	273	1167	214	54	124	63	17
650 ppmv	164	791	45	24	99	25	0
750 ppmv	130	693	0	0	89	0	0

* The OECD90 region includes the countries belonging to the OECD in 1990. The REF ("reforming economies") region aggregates the countries of the Former Soviet Union and Eastern Europe. The ASIA region represents the developing countries on the Asian continent. The ROW region covers the rest of the world, aggregating countries in sub-Saharan Africa, Latin America and the Middle East. For more details see SRES, 2000.

Figures

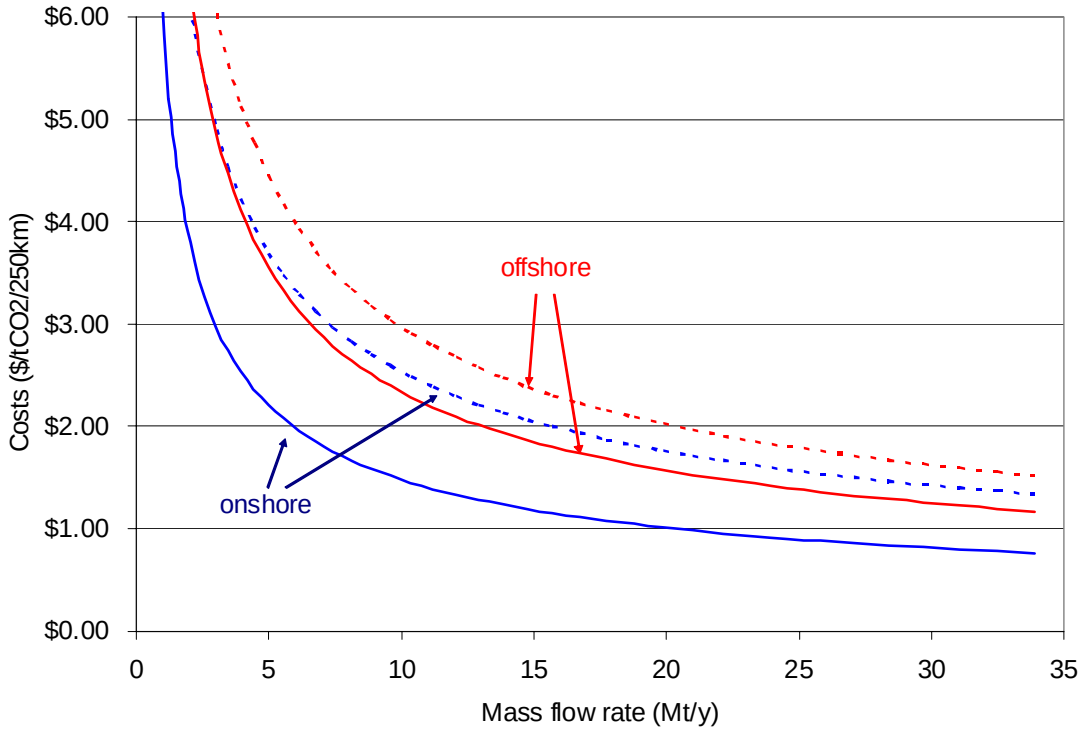

Figure 8.1. CO_2 transport costs range for onshore and offshore pipelines per 250 km, 'normal' terrain conditions. Indicated are high (dotted lines) and low range (solid lines). Data based on various sources (for details see Chapter 4).

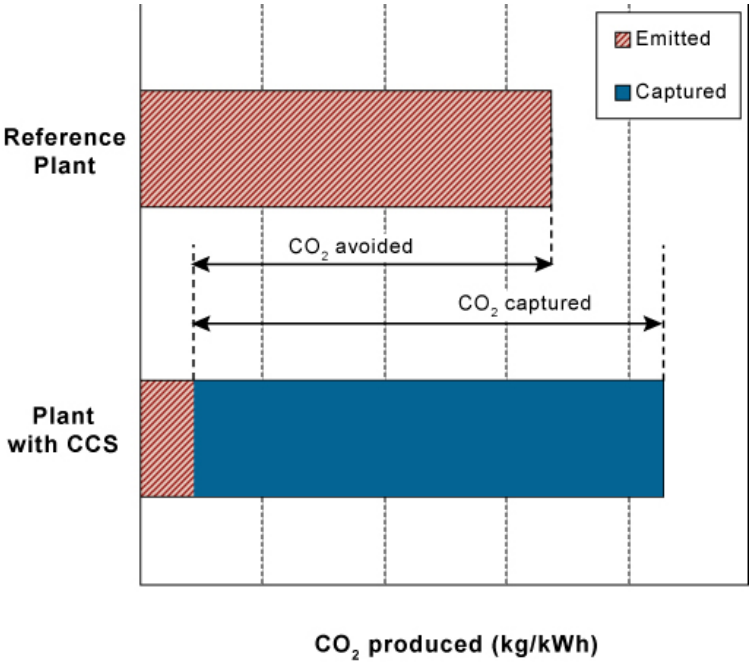

Figure 8.2. Difference between CO_2 captured and CO_2 avoided.

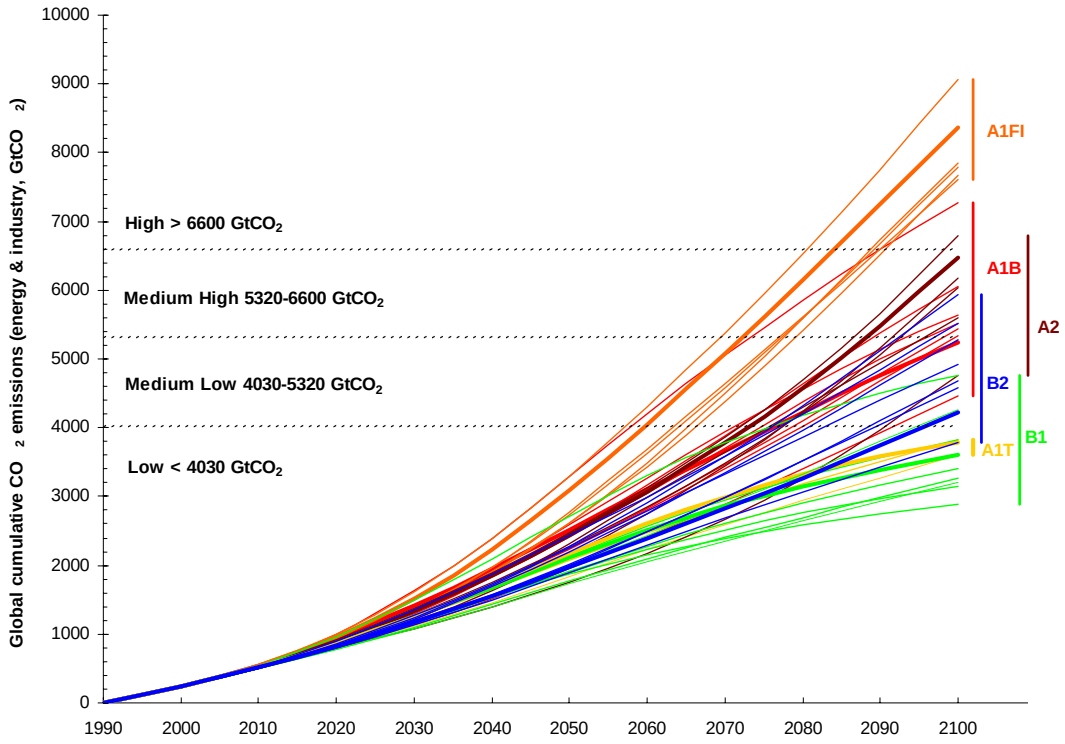

Figure 8.3. Annual and cumulative global emissions from energy and industrial sources in the SRES scenarios ($GtCO_2$). Each interval contains alternative scenarios from the six SRES scenario groups that lead to comparable cumulative emissions. The vertical bars on the right-hand side indicate the ranges of cumulative emissions (1990-2100) of the six SRES scenario groups.

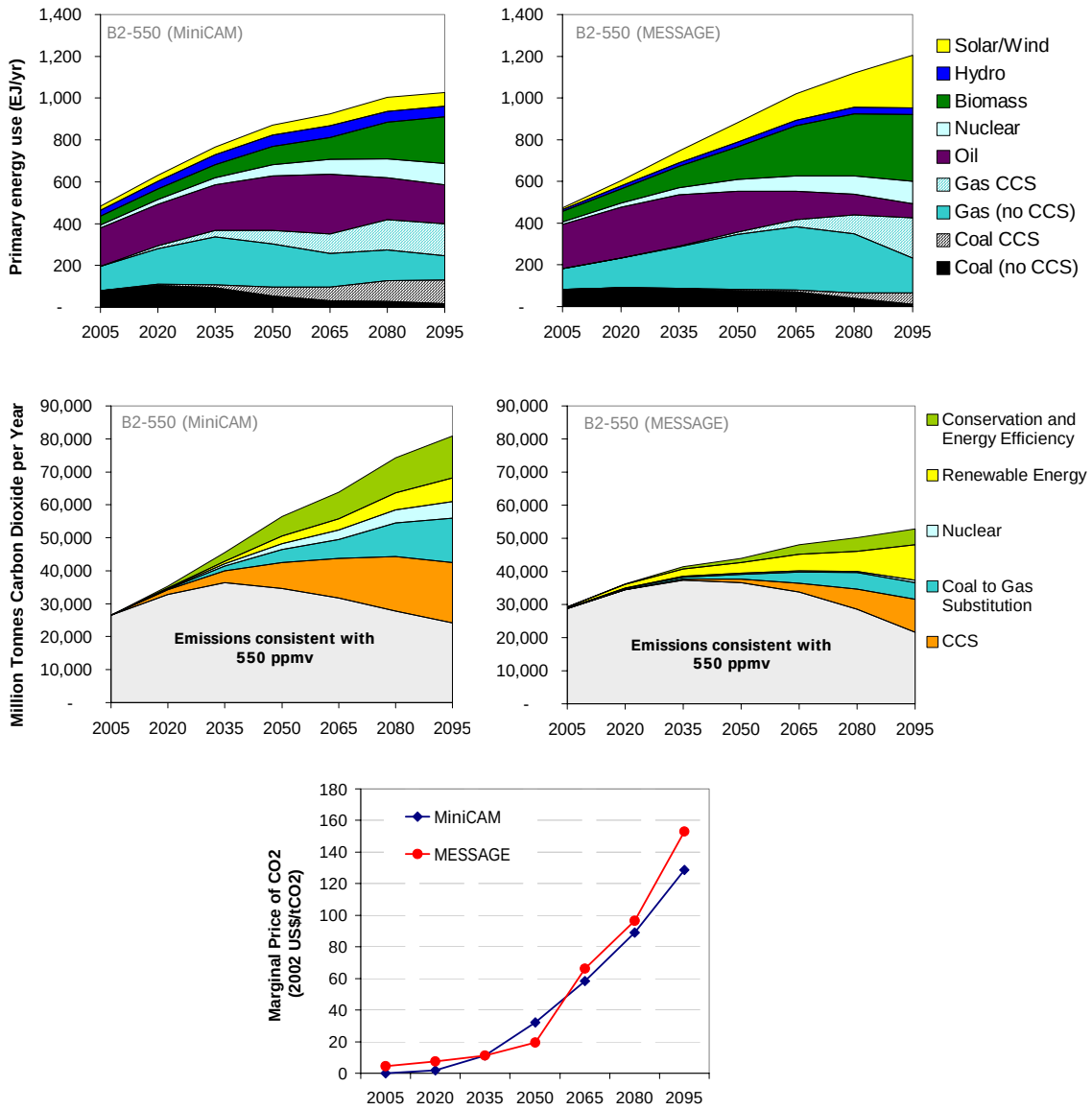

Figure 8.4. The set of graphs portray how two different Integrated Assessment models (MiniCAM and MESSAGE) project the development of global primary energy (upper panels) and the corresponding contribution of major mitigation measures (middle panels). The lower panel depicts the marginal carbon permit price in response to a modelled mitigation regime that seeks to stabilize atmospheric concentrations of CO_2 at 550 ppmv. Both scenarios adopt harmonized assumptions with respect to the main greenhouse gas emissions drivers consistent with the IPCC-SRES B2 scenario. (Source: Dooley, et al., 2004b and Riahi and Roehrl 2000).

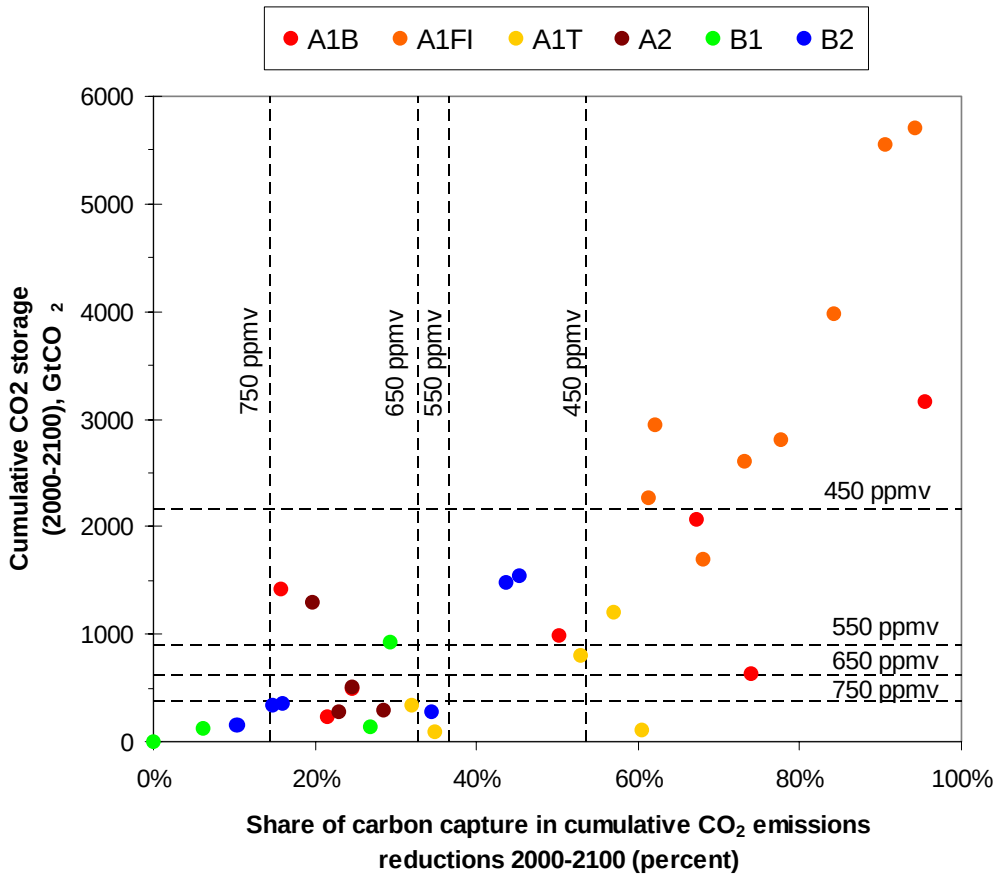

Figure 8.5. Relationship between (1) the imputed share of CCS in total cumulative emissions reductions in percent and (2) total cumulative CCS deployment in $GtCO_2$ (2000-2100). The scatter plots depict values for individual TAR mitigation scenarios for the six SRES scenario groups. Vertical dashed lines show the average share of CCS in total emissions mitigation across the 450 to 750 ppmv stabilization scenarios, and the dashed horizontal lines illustrate the scenario's average cumulative storage requirements across 450 to 750 ppmv stabilization.

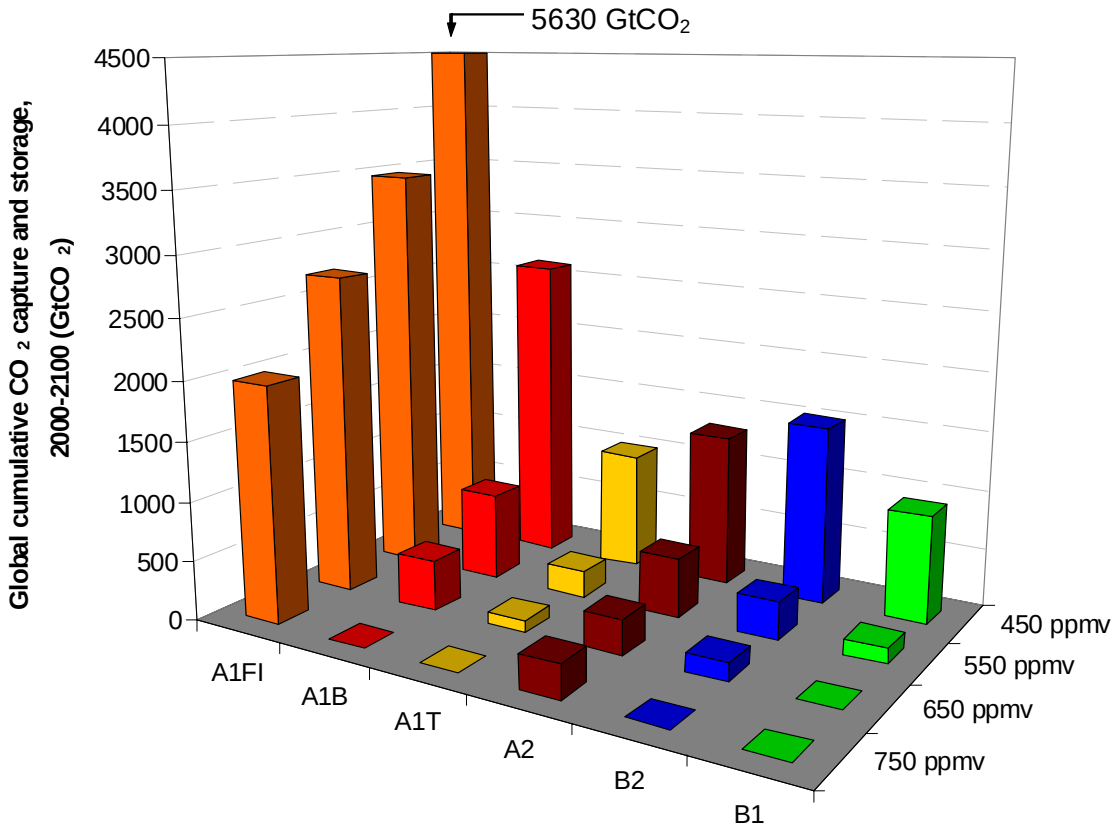

Figure 8.6. Global cumulative CO_2 storage (2000-2100) in the IPCC TAR mitigation scenarios for the six SRES scenario groups and CO_2 stabilization levels between 450 and 750 ppmv. Values refer to averages across scenario results from different modelling teams. The contribution of CCS increases with the stringency of the stabilization target and differs considerably across the SRES scenario groups.

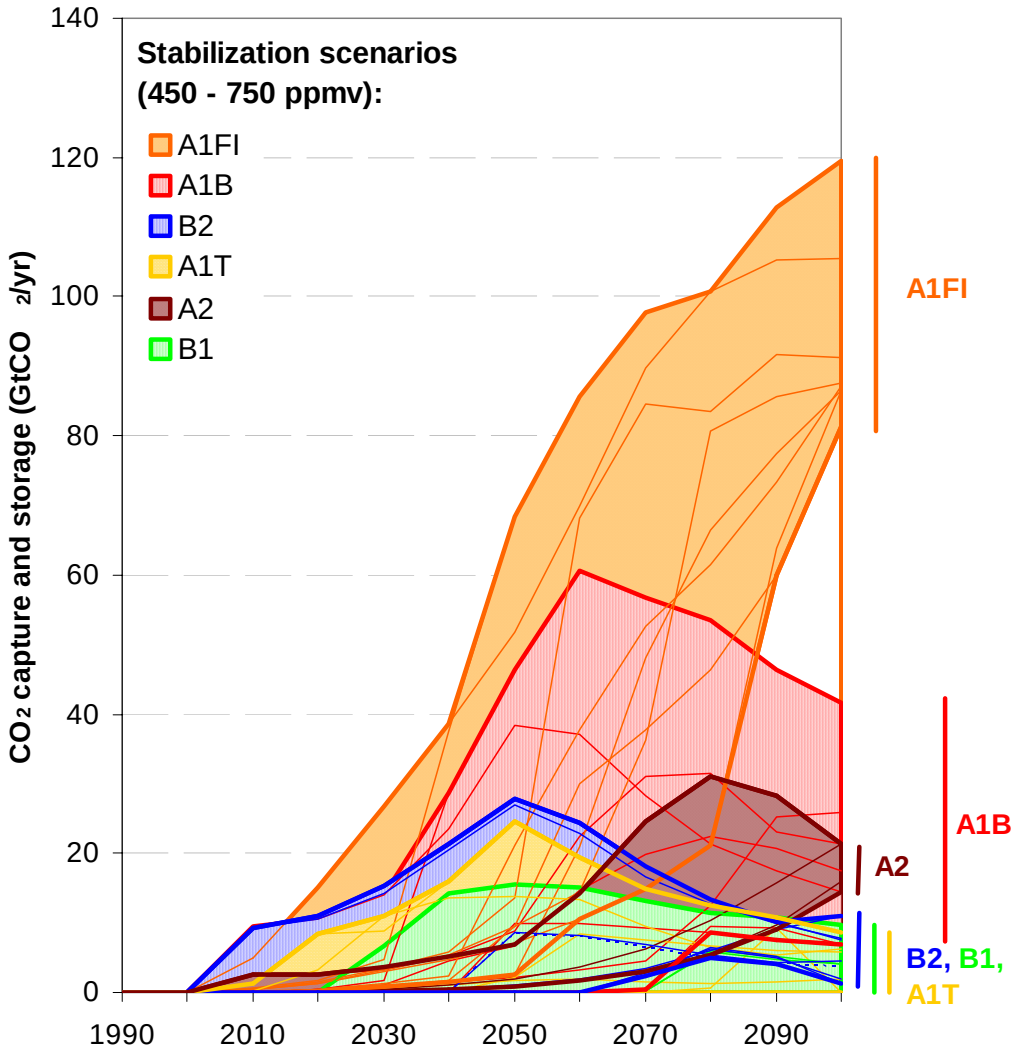

Figure 8.7. Deployment of CCS systems as a function of time from 1990 to 2100 in the IPCC TAR mitigation scenarios aiming at the stabilization of atmospheric CO_2 concentrations between 450 to 750 ppmv. Coloured thick lines show the minimum and maximum contribution of CCS for each SRES scenario group, and thin lines depict the contribution of individual scenarios. Vertical axes on the right hand side illustrate the range of CCS deployment across the stabilization levels for each SRES scenario group in the year 2100.

9. Implications of Carbon Dioxide Capture and Storage for Greenhouse Gas Inventories and Accounting

Coordinating Lead Authors
BALGIS OSMAN-ELASHA (SUDAN), RIITTA PIPATTI (FINLAND)

Lead Authors
William Kojo Agyemang-Bonsu (Ghana), A.M. Al-Ibrahim (Saudi Arabia), Carlos Lopez (Cuba), Gregg Marland (United States), Huang Shenchu (China), Oleg Tailakov (Russian Federation)

Review Editors
Takahiko Hiraishi (Japan), José Domingos Miguez (Brazil)

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Executive Summary

This Chapter addresses how methodologies to estimate and report the reduced/avoided greenhouse gas emissions from the main options for CO_2 capture and storage systems could be included in national greenhouse gas inventories, and in accounting schemes like the Kyoto Protocol.

The *IPCC Guidelines* and Good Practice Guidance reports (*GPG2000* and *GPG-LULUCF*) [1] are used in preparing national inventories under the UNFCCC. These guidelines do not specifically address CO_2 capture and storage, but the general framework and concepts could be applied also to CO_2 capture and storage systems. The IPCC Guidelines give guidance for reporting of actual annual emissions, by gas and by sector. The amount of CO_2 captured and stored can be measured, and could be reflected in the relevant sectors and categories producing the emissions, or by creating new specific categories for CO_2 capture, transportation and storage in the reporting framework. In the first option, CO_2 capture and storage would be treated as a mitigation measure and, for example, power plants with CO_2 capture or use of decarbonized fuels would have lower emissions factors (kg CO_2/kg fuel used) than conventional systems. In the second option, the captured and stored amounts would be reported as removals (sinks) for CO_2. In both options, the emissions from fossil fuel use due to the additional energy requirements in the capture, transportation and injection processes would be covered by the current methodologies. They would, however, not be allocated to the CO_2 capture and storage system under the current framework.

Methodologies to estimate, monitor and report physical leakage from the storage options would need to be developed. Fugitive emissions from capture, transportation and injection processes would also need some additional guidance specific to the systems. Chemical fixation and industrial use of CO_2 could conceptually follow a similar scheme. However, detailed methodologies would need to be developed for the specific processes.

Quantified commitments, emission trading or other similar mechanisms need clear rules and methodologies for accounting for emissions and removals. Lack of knowledge of the rate of physical leakage from the different storage options, including possibilities of accidental releases, over a very long time period (issues of permanence and liability), implications of the additional energy requirements of the options, and cases where the capture and storage of CO_2 cross the traditional accounting boundaries (issues of liability and economic leakage) are challenges for the accounting frameworks.

The literature on accounting for the potential impermanence of stored CO_2 is focused on sequestration in the terrestrial biosphere. Although sequestration in the terrestrial biosphere is notably different from CO_2 capture and storage in oceans or in geologic reservoirs (with respect to ownership; the role of management, measurement and monitoring; expected rate of physical leakage; modes of potential physical leakage; and assignment of liability), there are similarities as well. Accounting approaches, such as discounting, the ton-year approach, and rented or temporary credits, are discussed. Ultimately, political processes will decide the value of temporary storage and the allocation of responsibility for stored carbon. Precedents set by international agreements on sequestration in the terrestrial biosphere provide some guidance, but there are important differences that will have to be considered.

[1] Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 1997) – abbreviated as *IPCC Guidelines* in this chapter; IPCC Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories (IPCC 2000) – abbreviated as *GPG2000*; and IPCC Good Practice Guidance for Land Use, Land-Use Change and Forestry (IPCC 2003) – abbreviated as *GPG-LULUCF*.

9.1 Introduction

CO_2 capture and storage (CCS) can take a variety of forms. This chapter discusses how the main CCS systems, as well as carbon mineralization and industrial uses of CO_2, described in the previous chapters, could be incorporated into national greenhouse gas inventories and accounting schemes. Inventory or accounting issues specific to enhanced oil recovery or enhanced coal bed methane are not addressed here.

The inclusion of CCS systems in national greenhouse gas inventories is discussed in Section 9.2 (Greenhouse Gas Inventories). The section gives an overview of the existing framework, the main concepts and methodologies used in preparing and reporting national greenhouse gas emissions and removals. The section aims to identify inventory categories under which the CCS systems could be reported. Additionally, it aims to identify areas where existing methodologies could be used for including these systems in the inventories, and areas where new methodologies (including emission/removal factors and uncertainty estimates) would need to be developed. The treatment of CCS in corporate or company reporting is beyond the scope of the chapter.

Issues related to accounting[2] under the Kyoto Protocol; or under other similar accounting schemes that would limit emissions, provide credits for emissions reductions, or encourage emissions trading; are addressed in Section 9.3 (Accounting Issues). The section addresses issues that could warrant special rules and modalities in accounting schemes due to the specific features of CCS systems, such as the permanence of storage of CO_2 and liability issues related to transportation and storage in international territories and across national borders. Specific consideration is also given to CCS systems in relation to the mechanisms of the Kyoto Protocol (Emission Trading, Joint Implementation and the Clean Development Mechanism).

9.2 National Greenhouse Gas Inventories

Information on pollutant emissions is usually compiled in "emission inventories". The emissions are listed by pollutants, sectors, source categories, etc., and are compiled for a specified geographic area and interval of time. A wide variety of emission inventories exist and these are prepared for a variety of different purposes. Among the commitments in the United Nations' Framework Convention on Climate Change (UNFCCC, 1992) all Parties, taking into account their common but differentiated responsibilities, and their specific national and regional development priorities, objectives and circumstances, shall: *"Develop, periodically update, publish and make available to the Conference of the Parties, national inventories of anthropogenic emissions by sources and removals by sinks of all greenhouse gases not controlled by the Montreal Protocol, using comparable methodologies to be agreed upon by the Conference of the Parties".*[3]

Industrialized countries (so-called Annex I Parties) are required to do this reporting on an annual basis and developing countries (so-called non-Annex I Parties) are to report their greenhouse gas emissions and removals to the Convention periodically, as part of their National Communications to the UNFCCC. The national greenhouse gas inventories are prepared using the methodologies in the *IPCC Guidelines* as complemented by the *GPG2000* and G*PGLULUCF*, or methodologies that are consistent with these. All anthropogenic greenhouse gas emissions by sources and removals by

[2] "Accounting" refers to the rules for comparing emissions and removals as reported with commitments. In this context, "estimation" is the process of calculating greenhouse gas emissions and removals, and "reporting" is the process of providing the estimates to the UNFCCC (IPCC 2003).

[3] Commitment related to the Articles 4.1 (a) and 12.1 (a) of the United Nations Framework Convention of Climate Change (UNFCCC).

sinks not covered by the Montreal Protocol should be reported in the national greenhouse gas inventories. The national greenhouse gas inventories by Annex I Parties are reviewed by expert review teams, coordinated by the UNFCCC Secretariat, to ensure high quality and accuracy of the inventories. The review reports are published on the UNFCCC website[4].

The rules and modalities for accounting are elaborated under the Kyoto Protocol (UNFCCC, 1997) and the Marrakech Accords[5] (UNFCCC, 2002). The Kyoto Protocol specifies emission limitation or reduction commitments of the Annex I Parties for six gases/gas groups: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride (SF_6).

CO_2 capture and storage are practiced on a very small scale at present. CCS projects have not generally been described in the national inventory reports of the countries where they take place. An exception is the Sleipner CO_2 capture and storage project, which is included in Norway's inventory report.[6] Norway gives information on the annual captured and stored amounts, as well as on the amounts of CO_2 that escape to the atmosphere during the injection process (the amounts have varied from negligible to about 0.8% of the captured amount). The escaping CO_2 emissions are included in the total emissions of Norway. Monitoring of the spread of the CO_2 in the storage reservoir has been done using seismic methods. No physical leakage has been detected. An uncertainty estimate has not been performed but it is expected to be done when more information is available from the monitoring program of the project.

The scarce reporting of current CCS projects is due largely to the small number and small size of industrial CCS projects in operation, as well as to the lack of clarity in the reporting methodologies.

9.2.1 Revised 1996 IPCC Guidelines and IPCC Good Practice Guidance

The reporting guidelines under the UNFCCC[7], and under the Kyoto Protocol as specified in the Marrakech Accords, require that Annex I Parties use the *IPCC Guidelines*[1], as elaborated by the *GPG2000*[1], in estimating and reporting their national greenhouse gas inventories. The use of the *GPG-LULUCF*[1] will start in the year 2005 with a one year trial period[8]. Non-Annex I Parties also use the *IPCC Guidelines* in their reporting, and their use of the *GPG2000* and *GPG-LULUCF* reports is encouraged.[9] The main reporting framework (temporal, spatial and sectoral) and the guiding principles of the *IPCC Guidelines* and good practice guidance reports are given in Box 9.1.

The IPCC Guidelines will be revised and updated by early 2006[10]. In the draft outline for the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, CO_2 capture and storage are mentioned in a footnote in the Energy Sector: *"It is recognized that CO_2 capture and storage is an important emerging issue in inventory development. The coverage of CO_2 storage in this report will be closely*

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4 http://unfccc.int

5 The Marrakech Accords refer to the Report of the Conference of the Parties of the UNFCCC on its seventh session (COP7), held in Marrakech 29 October to 10 November 2001.

6 Norway's inventory report can be found at http://cdr.eionet.eu.int/no/un/UNFCCC/envqh6rog.

7 FCCC/CP2002/7/Add.2: Annexes to Decision 17/CP.8 Guidelines for the preparation of national communications from Parties not included in Annex I to the Convention and 18/CP.8 Guidelines for the preparation of national communications by Parties included in Annex I to the Convention, part I: UNFCCC reporting guidelines on annual inventories.

8 FCCC/SBSTA/2003/L.22 and FCCC/SBSTA/2003/L.22/Add.1.

9 FCCC/CP/2002/7/Add.2.

10 http://www.ipcc.ch/meet/session21.htm: IPCC XXI/Doc.10.

coordinated with progress on IPCC SR on CO_2 capture and storage. CO_2 capture activities will be integrated as appropriate into the methods presented for source categories where it may occur."

Box 9.1. Main reporting framework (temporal, spatial and sectoral) and guiding principles of the IPCC Guidelines and good practice guidance reports.

The IPCC methodologies for estimating and reporting **national** greenhouse gas inventories are based on **sectoral** guidance for reporting of actual emissions and removals of greenhouse gases by gas and **by year**. The *IPCC Guidelines* give the framework for the reporting (sectors, categories and sub-categories), default methodologies and default emission/removal factors (the so-called Tier 1 methodologies) for the estimation. Higher tier methodologies are based on more sophisticated methods for estimating emissions/removals and on the use of national or regional parameters that accommodate the specific national circumstances. Higher tier methodologies are not always described in detail in the IPCC Guidelines. The use of transparent and well-documented national methodologies consistent with those in the *IPCC Guidelines* is encouraged.

The Good Practice Guidance (GPG) reports facilitate the development of inventories in which the emissions/removals are not over- or underestimated, so far as can be judged, and in which the uncertainties are reduced as far as practicable. Further aims are to produce transparent, documented, consistent, complete, comparable inventories, which are i) assessed for uncertainties, ii) subject to quality assurance and quality control, and iii) efficient in the use of resources. The GPG reports give guidance on how to choose the appropriate methodologies for specific categories in a country, depending on the importance of the category (so-called key category analysis is used to determine the importance) and on the availability of data and resources for the estimation. Decision trees guide this choice of the estimation method most suited to the national circumstances. The category-specific guidance linked to the decision trees also provides information on the choice of emission factors and activity data. The GPG reports give guidance on how to meet the requirements of transparency, consistency, completeness, comparability, and accuracy required by the national greenhouse gas inventories.

The **Sectors** covered in the *IPCC Guidelines* are: (i) Energy, (ii) Industrial Processes, (iii) Solvent and Other Product Use, (iv) Agriculture, (v) Land Use Change and Forestry, (vi) Waste and (vii) Other. The use of the seventh sector, "Other", is discouraged: *"Efforts should be made to fit all emission sources/sinks into the six categories described above. If it is impossible to do so, however, this category can be used, accompanied by a detailed explanation of the source/sink activity" (IPCC 1997).*

9.2.2 Methodological Framework for CO_2 Capture and Storage Systems in National Greenhouse Gas Inventories

In this section alternatives for inclusion of CCS systems in national greenhouse gas inventories are analysed using the current methodological framework as the basis. The total chain from capture to storage (geological and ocean storage) is addressed. Two main options to incorporate the CCS systems into national greenhouse gas inventories are identified:

- Source reduction: To evaluate the CCS systems as mitigation options to reduce emissions to the atmosphere.
- Sink enhancement: To evaluate the CCS systems using an analogy with the treatment made to CO_2 removals by sinks in the sector Land Use, Land-Use Change and Forestry. A balance is made of the CO_2 emissions and removals to obtain the net emission or removal. In this option, removals by sinks are related to the CO_2 storage.

In both options, the estimation methodologies could be developed to cover most of the emissions that take place in the CCS system (see Figure 9.1), and the reporting could be done using the current framework available for the preparation of national greenhouse gas inventories.

Figure 9.1. A simple flow diagram showing possible CO_2 emission sources during different phases of the CO_2 capture and storage chain.

In the first option reduced emissions could be reported in the category where the capture takes place. For instance, reporting of capture in power plants could be done using lower emission factors than for plants without CCS. This could reduce the transparency of the reporting and make review of the overall impact on emissions more difficult, especially if the capture process and emissions from transportation and storage are not linked. This would be emphasized in cases where transportation and storage would include captured CO_2 from many sources, or when these would take place across national boarders. An alternative would be to track CO_2 flows through the entire capture and storage system so that it was transparent how much CO_2 was produced, how much was actually emitted to the atmosphere at each process stage, and how much CO_2 was transferred to storage. It is this latter approach that appears fully transparent and yet is consistent with earlier UNFCCC agreements, and is described in the remainder of this chapter.

In the second option the impact of the CCS system would be reported as a sink. For instance, reporting of capture in power plants would not alter the emissions from the combustion process but the stored amount of CO_2 would be reported as a removal in the inventory. The application of the second option would require the adoption of new definitions not available in the UNFCCC or in the current methodological framework for the preparation of inventories. The UNFCCC (1992) defines a sink as "any process, activity or mechanism which removes a greenhouse gas, an aerosol, or a precursor of a greenhouse gas **from the atmosphere**". Although "removal" was not included explicitly in the UNFCCC definitions, it appears associated with the "sink" concept. CCS[11] systems do not meet the UNFCCC definition for a sink, but given that the mentioned definition was agreed without having the CCS systems in mind, it is likely that this obstacle could be solved (Torvanger et al., 2005).

General issues of relevance to the CCS systems include the system boundaries (sectoral, spatial and temporal). The system boundaries will have different importance depending on the specific CCS systems and the specific phases of the systems. The basic methodological approaches for the various system components, as well as the status of the methods and the availability of data for these, are discussed below. Chemical fixation and industrial use of CO_2 are addressed separately.

- Sectoral boundaries: The draft outline for the *2006 IPCC Guidelines* (see Section 9.2.1) says that "CO_2 capture activities will be integrated as appropriate into the methods presented for source/sink categories where they may occur". This approach is followed here when addressing the sectors under which the specific phases of the CCS systems could be reported. The reporting of the emissions/removals associated with CO2 capture, transportation, injection and storage processes should be described clearly to fulfil the requirement of transparent reporting.
- Spatial boundaries: National inventories include greenhouse gas emissions and removals taking place within national (including administered) territories and offshore areas over which that country has jurisdiction. Some of the emissions and removals of CCS systems could happen

[11] Some few cases are nearer to the "sink" definition. For example, mineralization can also include fixation from the atmosphere.

outside of the areas under the jurisdiction of the reporting country, an aspect that requires additional consideration and is addressed mainly in Section 9.3.

- Temporal boundaries: Inventories are prepared on a calendar year basis. Some aspects of CCS systems (like the amount of CO2 captured or fugitive emissions from transportation) could be easily incorporated into an annual reporting system (yearly estimates would be required). On the other hand, other emissions (e.g., physical leakage of CO2 from geological storage) can take place a very long time after the injection activity was completed - time frames range from hundreds to even millions of years (see further discussion in Section 9.3).

Table 9.1 lists potential sources and emissions of greenhouse gases in the different phases of a CCS system and their relationship with the framework for the reporting (sectors, categories and sub-categories) of the *IPCC Guidelines*. The relative importance of these potential sources for the national greenhouse gas inventory can vary from one CCS project to another depending on factors such as capture technologies and storage site characteristics. Emissions of some of these sources are probably very small, sometimes even insignificant, but to guarantee an appropriate completeness[12] of the national inventory it is necessary to evaluate their contribution.

Table 9.1. Potential sources and emissions of greenhouse gases (GHG) in the different phases of a CCS system.

Some important considerations relative to the source categories and emissions included in Table 9.1 are the following:

- Capture, transportation and injection of CO_2 into storage require energy (the additional energy requirements are addressed in the previous chapters). The greenhouse gas emissions from this energy use are covered by the methodologies and reporting framework in the *IPCC Guidelines* and *GPG2000*. Additional methodologies and emission factors can be found in other extensive literature, e.g., EEA, 2001; US EPA (1995, 2000). In cases where capture processes take place at the fuel production site, the emissions from the fuel used in the capture process may not be included in the national statistics and additional methods to cover emissions from this source may be needed. In the current reporting framework the emissions from the additional energy requirements would not be linked to the CCS system.
- Fugitive emissions from CCS systems can take place during capture, compression, liquefaction, transportation and injection of CO_2 to the storage reservoir. A general framework for estimation of fugitive emissions is included in the *IPCC Guidelines* in the Energy sector. The estimation and reporting of fugitive emissions from CCS need further elaboration in the methodologies.
- The long-term physical leakage of stored CO_2 (escape of CO_2 from a storage reservoir) is not covered by the existing framework for the reporting of emissions in the *IPCC Guidelines*. Different potential options exist to report these emissions in the inventories (e.g., in the relevant sectors/categories producing the emissions initially, by creating a separate and new category under fugitive emissions, by creating a new category for the capture, transportation and/or storage industry, etc.).
- Application of CCS to CO_2 emissions from biomass combustion, and to other CO_2 emissions of biological origin (e.g., fermentation processes in the production of food and drinks) would require specific treatment in inventories. With regard to biomass fuels, it is generally assumed that combustion of biomass fuels results in zero net CO_2 emissions if the biomass fuels are

[12] Completeness means that an inventory covers all sources and sinks, as well as all gases, included in the IPCC Guidelines, as well as other existing relevant source/sink categories which are specific to individual Parties, and therefore may not be included in the IPCC Guidelines. Completeness also means full geographic coverage of sources and sinks of a Party (FCCC/CP/1999/7).

produced sustainably. In this case the CO_2 released by combustion is balanced by CO_2 taken up during photosynthesis. In greenhouse gas inventories the CO_2 emissions from biomass combustion are therefore not reported under Energy and any unsustainable production should be evident in the calculation of CO_2 emissions and removals in Land Use, Land-Use Change and Forestry Sector. Thus CO_2 capture and storage from biomass sources would be reported as negative CO_2 emissions.

9.2.2.1 Capture

The capture processes are well-defined in space and time and their emissions (from additional energy use, fugitives etc.) could be covered by the current national and annual inventory systems. The capture processes would result in reduced emissions from industrial plants, power plants and other sites of fuel combustion. For estimation purposes, the reduced CO_2 emissions could be determined by measuring the captured amount of CO_2 and subtracting this from the total amount of CO_2 produced (see Figure 8.2 in Chapter 8).

The total amount of CO_2, including emissions from the additional energy consumption necessary to operate the capture process, could be estimated using the methods and guidance in the *IPCC Guidelines* and *GPG2000*. The capture process could produce emissions of other greenhouse gases, like CH_4 from treatment of effluents (e.g., from amine decomposition). These emissions are not included explicitly in the *IPCC Guidelines* and *GPG2000*. Estimates on the significance of these emissions are not available, but they are likely to be small or negligible compared to the captured amount of CO_2.

Although it is not possible here to consider all the possible CCS systems, it is clear that some cases would require different approaches. For example, pre-combustion decarbonization in fuel production units presents some important differences compared to the post-combustion methods, and the simple estimation process described above might not be applicable. For example, the capture of CO_2 may take place in a different country than the one in which the decarbonized fuel is used. This would mean that the emissions associated with the capture process (possible fugitive CO_2 emissions from the process) would need to be estimated and reported separately from those resulting from the combustion process (see also Section 9.3 on issues relating to accounting and allocation of the emissions and emissions reductions).

9.2.2.2 Transportation

Most of the research efforts on CO_2 capture and storage systems are oriented toward the capture and storage processes - fugitive emissions from CO_2 transportation are often overlooked (Gale and Davison, 2002). Chapter 4 of this report addresses the transportation of CO_2 in pipelines and ships. Limited quantities of CO_2 could also be transported via railway or by trucks (Davison et al., 2001). The additional energy required for pipeline transport is mostly covered by the compression done at the capture site. Very long transportation distances may require additional compression during the transport phase. The emissions caused by fossil fuel use in transportation by ships, rail or trucks would be covered under the category on mobile combustion and other subcategories in the Energy sector. However, emissions from fuels sold to any means of international transport should, according to the current IPCC guidelines, be excluded from the national total emissions and be reported separately – as emissions from international bunkers. Emissions from international bunkers are not included in national commitments under the Kyoto Protocol (e.g. IPCC 1997 and 2000, see also Section 9.3).

Any fugitive emissions or accidental releases from transportation modes could be covered in the Energy sector under the category "Fugitive Emissions". CO_2 emissions from a pipeline can occur at

the intake side during pumping and compression, at the pipeline joints or at the storage place. Surface, underground and sub-sea pipelines could have different emission rates. The current IPCC methodologies do not give explicit guidance for CO_2 transportation in pipelines, but do include methodology for natural gas pipelines. There is a distinction to be made between leakage during normal operation and CO_2 losses during accidents or other physical disruptions. As described in Chapter 4, Gale and Davison (2002) point out that statistics on the incident rate in pipelines for natural gas and CO_2 varied between 0.00011 to 0.00032 incidents/km year. However, as an analogy of CO_2 transportation to natural gas transportation, Gielen (2003) reported that natural gas losses during transportation can be substantial.

Total emissions from pipelines could be calculated based on the net difference between the intake and discharge flow rates of the pipelines. Due to the fact that CO_2 is transported in pipelines as a supercritical or dense phase fluid, the effect of the surrounding temperature on the estimated flow rate would need to be taken into account. CO_2 may be transmitted from a cooler climate to a moderate or hot climate, and vice versa, and volumetric values would need to be corrected accordingly. In some cases, fugitive losses could be lower than metering accuracy tolerances. Hence, all metering devices measuring CO_2 export and injection should be to a given standard and with appropriate tolerances applied. It is imperative to note that metering uncertainties may prohibit measurement of small quantities of losses during transportation. For transportation by CO_2 pipeline across the borders of several countries, emissions would need to be allocated to the countries where they occur.

No methodologies for estimation of fugitive emission from ships, rail or road transportation are included in the IPCC Guidelines.

9.2.2.3 Storage

Chapters 5 and 6, on geological and ocean storage, give some estimates on CO_2 emissions (physical leakage rates) from the storage options. Physical leakage rates are estimated to be very small for geological formations chosen with care. In oil reservoirs and coal seams the storage times could be significantly altered if exploitation or mining activities in these fields would be undertaken after the CO_2 storage took place. Some of the CO_2 injected into oceans would be released back into the atmosphere over a period of hundreds to thousands of years, depending on the depth and location of injection.

The amount of CO_2 injected or stored could be easily measured in many CCS systems. Estimation of physical leakage rates would require new methodologies to be developed. Very limited data are available in relation to the physical leakage of CO_2.

Despite the essential differences in the nature of the physical processes of CO_2 retention in oceans, geological formations, saline aquifers and mineralized solids; the mass of CO_2 stored over a given time interval by these types of storage can be defined by the Equation 1.

$$CO_2 stored = \int_o^T (CO_2 injected(t) - CO_2 emitted(t))dt \qquad (1)$$

where t is time and T is the length of the assessment time period.

Implementation of this simple equation would require estimates or measurements on the injected CO_2 mass and either default values of the amount of CO_2 emitted from the different storage types, or rigorous source-specific evaluation of the mass of escaped CO_2. Application of this approach would be possible when accurate measurements of mass of injected and escaped CO_2 are applied on site. Thus for monitoring of possible physical leakage of CO_2 from geological formations, direct

measurement methods for CO_2 detection, geochemical methods and tracers, or indirect measurement methods for CO_2 plume detection could be applied (see Chapter 5, Section 5.6 Monitoring and Verification Technology).

Physical leakage of CO_2 from storage could be defined as follows (Equation 2):

$$\textit{Emissions of } CO_2 \textit{ from Storage} = \int_0^T m(t)dt \qquad (2)$$

where m(t) is the mass of CO_2 emitted into the atmosphere per unit of time and T is the assessment time period. This addresses physical leakage that might occur in a specific timeframe after the injection, perhaps far into the future. The issue is discussed further in Section 9.3.

9.2.2.4 Chemical fixation

Chemical fixation of CO_2 captured from power plants and industrial processes is addressed in Chapter 7. These processes are still under development and aim at permanent fixation of the CO_2 in a solid mineral phase. There is no discussion in the literature about possible modes and rates of physical leakage of CO_2 from mineral trapping, probably because investigations in this field have been largely of theoretical character (e.g. Goldberg et al., 2000). However, the produced carbonate would be unlikely to release CO_2 after mineralization. Some amount of gas could, however, escape into the atmosphere before and during the mineralization process.

The actual net benefits of mineralization processes would depend on the total energy use of the chain from capture to storage, and the general framework discussed above for CCS systems can be applied also in inventorying emissions from these processes. The emissions from the additional energy requirements would be seen in the energy sector under the current reporting framework. The amount of CO_2 captured and mineralized could be reported in the category where the capture takes place or as a specific category addressing mineralization, or in the sector "Other".

9.2.2.5 Industrial uses

Most industrial uses of CO_2 result in release of the gas back to the atmosphere, often after a very short time period. These systems may not require any change in the inventory systems due to the short “storage times”, as long as the inventory system is robust enough to avoid possible double counting or omission of the emissions. The benefits of these systems are related to the systems they substitute for, and the relative net efficiencies of the alternate systems. Comparison of the systems would need to take into account the whole cycle from capture to use of CO_2. As an example, methanol production by CO_2 hydrogenation could be a substitute for methanol production from fossil fuels, mainly natural gas. The impacts of the systems are in general covered by current inventory systems, although they are not addressed explicitly, because the emissions and emission reductions are related to relative energy use (reduction or increase depending on the process alternatives).

In cases, where the industrial use of CO_2 would lead to more long term storage of carbon in products, the inventory methodologies would need to be tailored case by case.

9.2.3 Monitoring, verification and uncertainties

The IPCC Guidelines and good practice reports give guidance on monitoring, verification and estimation of uncertainties, as well as on quality assurance and quality control measures. General guidance is given on how to plan the monitoring, what to monitor and how to report on results. The purpose of verifying national inventories is to establish their reliability and to check the accuracy of the reported numbers by independent means.

Section 5.6, Monitoring and Verification Technology, assesses the current status of monitoring and verification techniques for CCS systems. The applicability of the monitoring techniques as well as associated detection limits and uncertainties vary much depending on the type and specific characteristics of the CCS projects. The experiences from monitoring existing CCS projects are still too scarce to allow for conclusions on the physical leakage rates.

Reporting of uncertainties in the emission and removal estimates, and how they have been derived, is an essential part of national greenhouse gas inventories. Uncertainty estimates can be based on statistical methods when measured data are available, or on expert judgement. No information on uncertainties related to emissions from different phases of CCS systems was available. In Section 5.7.3 the probability of release from geological storage is assessed based on data from analogous natural or engineered systems, fundamental physical and chemical processes, as well as from experience with current geological storage projects. The probabilities of physical leakage are estimated to be small and the risks are mainly associated with leakage from well casings of abandoned wells.

9.3 Accounting Issues

One of the goals of an accounting system is to ensure that carbon dioxide capture and storage projects produce real and quantifiable environmental benefits. One ton of CO_2 permanently stored has the same benefit in terms of atmospheric CO_2 concentrations as 1 ton of CO_2 emissions avoided, but 1 ton of CO_2 temporarily stored has less value than 1 ton of CO_2 emissions avoided, and this difference can be reflected in the accounting system. Accounting for CO_2 capture and storage may have to go beyond measuring the amount of CO_2 stored in order to ensure the credibility of storage credits and that credits claimed are commensurate with benefits gained. CO_2 storage should not avoid properly accounting for emissions because emissions are moved to other times, other places, or other sectors. And yet, Kennett (2003) notes that if there is benefit to potentially permanent, or even to known temporary, storage; accounting systems should contribute to their credibility and transparency while minimizing transaction costs.

In a political environment where only some parties have commitments to limit greenhouse gas emissions and where emissions from all sources are not treated the same, the amount by which emissions are reduced may not be equal to the amount of CO_2 stored. Differences can occur because CO_2 can be captured in one country but released in another country or at a later time. Also, CO_2 capture and storage require energy and likely additional emissions of CO_2 to produce this additional energy. Yoshigahara (2004) notes that emission reduction through CCS technology differs from many other modes of emission reduction because, although the former avoids the release of CO_2 to the atmosphere, it creates the long-term possibility that the stored CO_2 could eventually flow to the atmosphere through physical leakage.

In this Chapter, the general term “leakage” is used in the economist’s sense, to describe displacement of greenhouse gas emissions beyond the boundaries of the system under discussion. The term “physical leakage” is used to refer to actual escape of CO_2 from a storage reservoir. As discussed above, some of these physical leakage effects and the additional energy requirements will be reported within standard, national reporting procedures for greenhouse gas emissions. Additional complexities arise when new or unexpected sources of emissions occur (for example, if CO_2 injected into an uneconomic coal seam forces the release of methane from the seam), in different countries (for example, if CO_2 is captured in one country but released in another), or at later times

(for example, if CO_2 is captured during one time period and physically leaked to the atmosphere at a later time).

The problems of economic leakage are not unique to CCS systems, but the problems of physical leakage are unique to CCS. In particular, when emissions inventories are done by country and year they may fail to report emissions that are delayed in time, displaced to other countries or to international waters, or that stimulate emissions of other greenhouse gases that are not identified as sources or for which methodologies have not been developed.

In this section ideas on the issues involved in accounting are summarised for the stored CO_2 of CCS systems. The consequences for greenhouse gas mitigation efforts are discussed, and some ideas on alternative accounting strategies that might be used to address them are presented. Figure 9.2 provides a simple flow diagram of how capture and storage of CO_2 emissions can create flows of greenhouse gases that transcend traditional accounting boundaries and the possibility that emissions might escape reporting because they occur outside of the normal system boundaries (either sectoral, national, or temporal) of reporting entities.

Concern about the displacement of emissions across national boundaries is a consequence of the political and economic constructs being developed to limit greenhouse gas emissions. Most notably, the Kyoto Protocol imposes limits on greenhouse gas emissions from developed countries and from countries with economies in transition, but no such limits on emissions from developing countries or international transport.

Concern about the displacement of emissions across temporal boundaries is essentially the widely posed question: "if we store carbon away from the atmosphere, how long must it be stored?" Alternatively, Herzog et al. (2003) phrase the same question "What is the value of temporary storage?"

Concern about leakage among countries, sectors, or gases; or physical leakage from reservoirs is largely about the completeness and accuracy of emissions accounting. Kennett (2003), for example, emphasizes the importance of "establishing general rules and procedures to simplify transactions, and increasing certainty by defining legal rights and by providing dispute resolution and enforcement procedures" and of ensuring the credibility of sinks-based emissions offsets or storage-based emissions reductions. The operation of a market requires clearly defined rights (i.e. who has the rights to the carbon stored), what those rights entail, how those rights can be transferred, and liability and remedies in the event of unanticipated release (Kennett, 2003, p. 259). The accounting and certification systems will be at the core of establishing rights, liabilities, and markets. And yet a well designed accounting system should not lead to transaction costs that unnecessarily discourage meritorious activities.

Figure 9.2. A simple flow diagram on how CO_2 capture and storage could transcend traditional accounting boundaries.

9.3.1 Uncertainty, Non-Permanence and Discounting Methodology

9.3.1.1 Dealing with the impermanence of carbon dioxide storage

Storage of CO_2 is not necessarily permanent. The possibility of physical leakage from storage reservoirs exists via (1) gradual and long-term release or (2) sudden release of CO_2 caused by disruption of the reservoir. There is very little literature on accounting for the potential

impermanence of CO_2 capture and storage. There is, however, a significant literature on accounting for the impermanence of CO_2 sequestration in the terrestrial biosphere. Although sequestration in the terrestrial biosphere is notably different from CO_2 storage in the ocean or in geologic reservoirs, there are similarities as well. It is clear that CO_2 stored in the terrestrial biosphere is subject to potential future release if, for example, there is a wildfire, the landowner changes management practices, or climate change renders the vegetative cover unsustainable. Although the risks of CO_2 loss from well-chosen geologic reservoirs are very different, such risks do exist. The literature suggests a variety of possible accounting strategies so that sequestration in the biosphere could be treated as the negative equivalent of emissions, sequestration could be shown in national emissions accounts and trading of emissions credits, and debits between parties could occur for sequestration activities in the terrestrial biosphere. Whether CCS is treated as a CO_2 sink or as a reduction in emissions, the issues of accounting for physical leakage from storage are similar.

Chomitz (2000) suggests that there are two primary approaches to accounting for stored CO_2: (1) acknowledge that CO_2 storage is likely not permanent, assess the environmental and economic benefits of limited-term storage, and allot credits in proportion to the time period over which CO_2 is stored, and (2) provide reasonable assurance of indefinite storage. Examples discussed for sequestration in the terrestrial biosphere include (under the first approach) ton-year accounting (described below); and (under the second approach) various combinations of reserve credits and insurance so that lost CO_2 is replaced by sequestration reserves or other permanent emissions reductions (for further discussion see Watson et al., 2000; Marland et al., 2001; Subak, 2003; Aukland et al., 2003; Wong and Dutschke, 2003; and Herzog et al., 2003). There are also proposals to discount credits so that there is a margin of conservativeness in the number of credits acknowledged. In the presence of these kinds of discussions and uncertainty, negotiations toward the Kyoto Protocol have chosen to place limits on the number of credits that can be claimed for some categories of terrestrial CO_2 sequestration during the Protocol's first commitment period (UNFCCC, 2002).

To illustrate the concept of allotting credits in proportion to storage time, we briefly elaborate on one alternative, the ton-year approach. The ton-year alternative for accounting would define an artificial equivalence so that capture and storage for a given time interval (for example, t years) would be equated with permanent storage. There are alternative ways for defining when the credits would become available, but typically capture and storage for 1 year would result in a number of credits which is equal to 1/t , and thus storage for t years would result in 1 full credit (Watson et al., 2000). A variety of constructs have been proposed for defining the number of years of storage that would be equated with permanent storage (see, for example, Marland et al., 2001) but, as Chomitz (2000) points out, despite being based on scientific and technical considerations, this equivalence is basically a political decision. Although ton-year accounting typifies the first approach, it has been subject to considerable discussion and the idea of expiring credits or rented temporary credits (Marland et el., 2001; Subak, 2003) is another derivative of Chomitz's first approach that has been further developed within negotiations on the Kyoto Protocol (Columbia, 2000; UNFCCC, 2002; UNFCCC, 2004). Temporary or rented credits would have full value over a time period defined by rule or by contract, but would result in debits or have to be replaced by permanent credits at expiration. In essence, credit for stored CO_2 would create liability for the possibility that the CO_2 was subsequently released or the commitment to storage was ended.

UNFCCC (2002), Marland et al. (2001), Herzog et al. (2003), and others agree that the primary issue for stored CO_2 is one of liability. They argue that if credit is given for CO_2 stored, there should be debits if the CO_2 is subsequently released. Physical leakage from storage and current emissions produce the same result for the atmosphere. Accounting problems arise if there is a transfer of

ownership or a transfer of stored CO_2 to a place or party that does not accept liability (e.g. if CO_2 is stored in a developing country without commitments under the Kyoto protocol) or if potential debits are transferred sufficiently far into the future that there can be little assurance that the systems and institutions of liability will still be in place if and when CO_2 is released. The system of expiring credits contained in the Marrakesh Accords for sequestration in the terrestrial biosphere fulfills the requirement of continuing liability and limiting these credits to 5 years provides reasonable assurance that the liable institutions will still be responsible. This arrangement also addresses one important concern of those who might host CO_2 storage projects, that they might be liable in perpetuity for stored CO_2. Under most proposals, the hosts for CO_2 storage would be liable for losses until credits expire and then liability would return to the purchaser/renter of the expiring credits. Kennett (2003) suggests that long-term responsibility for regulating, monitoring, certifying, and supporting credits will ultimately fall to governments (see also section 5.8.4 of this volume). With this kind of ultimate responsibility, governments may wish to establish minimum requirements for CCS reservoirs and projects (see Torvanger et al., 2005).

The published discussions of "permanence" have largely been in the context of sequestration in the terrestrial biosphere and it is not clear that the evolving conclusions are equally appropriate for CO_2 capture and storage in the ocean or in geologic reservoirs. There are important differences between the various modes of CO_2 capture and storage that may influence the accounting scheme chosen (see Table 9.2). An apparent distinction is that sequestration in the terrestrial biosphere involves initial release of CO_2 to the atmosphere and subsequent removal by growing plants, whereas storage in geologic reservoirs does not generally involve a release to the atmosphere and might be envisioned as a decrease in emissions rather than as a balancing of a source with a sink. In either case, however, one ends up with a mass of CO_2 that must be managed and isolated from the atmosphere. Of particular interest is the fact that for storage in the terrestrial biosphere it is most important to hold open the possibility that sequestration will be reversed because of human decisions on maintenance or priorities for resource management. Oceanic and geologic storage have very different implications for the time scale of commitments and for the role of physical processes vs. human decisions in potential physical releases.

Table 9.2. Differences in the forms of carbon storage that might influence the way accounting is conducted.

An important question for crediting CO_2 sequestration is whether future emissions have the same value as current emissions. Herzog et al. (2003) define a "sequestration effectiveness" as the net benefit from temporary storage compared to the net benefit of permanent storage, but this is a value that we cannot know in advance. Herzog et al. go one step further and argue that while CO_2 storage is not permanent, reducing emissions may not be permanent either – unless there is some backstop energy technology that will assure that all of fossil fuel resources are not eventually consumed. Stored CO_2 emissions are little different, according to Herzog et al., than fossil fuel resources left in the ground. On the other hand, most analysts assume that all fossil fuels will never be consumed so that refraining from emitting fossil-fuel CO_2 does not, like CO_2 storage, give rise directly to a risk of future emissions. Wigley et al. (1996) and Marland et al. (2001) argue that there is value in delaying emissions. Note that if storage for 100 years were to be defined as permanent, then virtually all carbon injected below 1500 m in the oceans would be considered to be permanent storage (Herzog et al., 2003). At the other temporal extreme, Kheshgi et al. (1994) point out that over the very long term of equilibration between the ocean and atmosphere (over 1000 years), capture and storage in the ocean will lead to higher levels of CO_2 in the atmosphere than without emissions controls, because of the additional energy requirements for operating the system. It is also true that chronic physical leakage over long times could increase the difficulty of meeting

targets for net emissions at some time in the future (see Hawkins, 2003; Hepple and Benson, 2003; and Pacala, 2003).

The fundamental question is then, how to deal with impermanent storage of CO_2. Although Findsen et al. (2003) detail many circumstances where accounting for CO_2 capture and storage is beginning or underway, and although the rates of physical leakage for well-designed systems may sometimes be in the range of the uncertainty of other components of emissions, the risks of physical leakage need to be acknowledged and there are a number of questions that remain to be answered. These include: how to deal with liability and the continuity of institutions in perpetuity; how to quantify the benefits of temporary storage; the needs in terms of monitoring and verification; whether or not there is a need for a reserve of credits or other ways to try to assure that losses will be replaced; whether or not there is a need for a system of discounting to consider expected or modeled duration of storage; the utility of expiring, temporary, or rented credits over very long time periods; whether there is a need to consider different accounting practices as a function of expected duration of storage or mode of storage; and the implications if storage in the terrestrial biosphere and in geologic formations may be sufficiently different that the former might be considered carbon management and the latter CO_2 waste disposal.

Ultimately the political process will decide the value of temporary storage and the allocation of responsibility for stored CO_2. Precedents set by international agreements on sequestration in the terrestrial biosphere provide some guidance, but there are important differences that will have to be considered. The reason for rules and policies is presumably to influence behaviour. Accounting rules for CO_2 storage can best influence permanence if they are aimed accordingly: at the liability for CO_2 stored in the terrestrial biosphere but at the initial design and implementation requirements for CO_2 capture and storage in the oceans or geologic reservoirs.

9.3.1.2 Attribution of Physical Leakage from Storage in International/Regional Territories or shared facilities and the use of engineering standards to limit physical leakage

The previous section deals largely with the possibility that CO_2 emissions stored now will be released at a later time, but it also introduces the possibility that emissions stored now will result in additional, current emissions in different countries or in different sectors. CO_2 injected into the ocean could leak physically from international waters. Accounting for stored CO_2 raises questions like responsibility for the emissions from energy used in transport and injection of CO_2, especially if transport and/or storage will be in a developing country or in international waters. Similarly, questions about the physical leakage of stored CO_2 will need to address where liability lies for current year physical leakage that occurs in developing countries or from international waters. These questions may be especially complex if multiple countries have injected CO_2 into a common reservoir such as the deep Atlantic Ocean or into a deep aquifer that lies under multiple countries or if, for example, multiple countries share a common pipeline for CO_2 transport

There may also be a need for international agreement on certification of sequestration credits or performance standards for sequestration projects – standards that would minimize the risk of leakage and maximize the time for CO_2 storage. Performance standards could minimize the possibility of parties looking for the least cost, lowest quality storage opportunities - opportunities most susceptible to physical leakage - when liability for spatial or temporal leakage is not clear. Performance standards could be used to limit the choice of technologies, the quality of operations, or the levels of measurement and monitoring.

9.3.2 Accounting issues related to Kyoto Mechanisms (JI[13] , CDM[14], and ET[15]

CO_2 capture and storage is not currently addressed in the decisions of the COP to the UNFCCC in relation to the Kyoto mechanisms. Little guidance has been provided so far by international negotiations regarding the methodologies to calculate and account for project-related CO_2 reductions from CCS systems under the various project-based schemes in place or in development. The only explicit reference to CCS in the Kyoto Protocol states that Annex I countries need to research, promote, develop and increasingly use CO_2 sequestration technologies[16]. The Marrakech Accords further clarify the Protocol regarding technology cooperation stating that Annex I countries should indicate how they give priority to co-operation in the development and transfer of technologies relating to fossil fuel that capture and store greenhouse gases (Paragraph 26, Decision 5/CP.7). No text referring explicitly to CCS project-based activities can be found in the CDM and JI-related decisions (Haefeli et al., 2004).

Haefeli et al. (2004) note further that CO_2 reporting schemes that include projects (i.e. the Chicago Climate Exchange and the EU Directive for establishing a Greenhouse Gas Emissions Trading Scheme (implemented in 2005) along with the EU Linking Directive (linking the EU Emissions Trading Scheme with JI and the CDM) do not yet explicitly address CCS in any form. The Kyoto Protocol encourages development of CO_2 sequestration technologies. At present it is unclear how CCS will be dealt with in practice. According to Haines et al (2004), the eligibility of CCS under CDM could be resolved in a specific agreement similar to that for land use, land-use change and forestry (LULUCF) activities. As with biological sinks, there will be legal issues as well as concerns with permanence and economic leakage, or emissions outside a system boundary. At the same time, CCS could involve a rather less complex debate because of the geological time scales involved. Moreover, Haefeli et al (2004) noted that guidelines on how to account for CO_2 transfers between countries would either need to be agreed under the UNFCCC or the Kyoto Protocol with special attention to the case where CO_2 is exchanged between an Annex I country and a non-Annex I country, and between an Annex I country party to the Kyoto Protocol and an Annex I country that has not ratified the Kyoto Protocol.

9.3.2.1 Emission Baselines

The term "baseline," mostly used in the context of project-based accounting, is a hypothetical scenario for what the greenhouse gas emissions would have been in the absence of a greenhouse gas reduction project or activity (WRI, 2004). Emission baselines form the basis from which net reductions (e.g., storage) of emissions from any project-based activity are calculated. Establishment of baselines is necessary to show the net benefits of emissions reductions. The important issue is to determine which factors need to be taken into account when developing an emissions baseline – and

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[13] Kyoto Protocol **Article 6.1** "For the purpose of meeting its commitments under Article 3, any Party included in Annex I may transfer to, or acquire from, any other such Party emission reduction units resulting from projects aimed at reducing anthropogenic emissions by sources or enhancing anthropogenic removals by sinks of greenhouse gases in any sector of the economy…"

[14] **Kyoto Protocol Article 12. 2**"The purpose of the clean development mechanism shall be to assist Parties not included in Annex I in achieving sustainable development and in contributing to the ultimate objective of the Convention, and to assist Parties included in Annex I in achieving compliance with their quantified emission limitation and reduction commitments under Article 3."

[15] **Kyoto Protocol Article 17** "The Conference of the Parties shall define the relevant principles, modalities, rules and guidelines, in particular for verification, reporting and accountability for emissions trading. The Parties included in Annex B may participate in emissions trading for the purpose of fulfilling their commitments under Article 3. Any such trading shall be supplemental to domestic actions for the purpose of meeting quantified emission limitation and reduction commitments under that Article."

[16] Article 2, 1(a) (iv) of the Kyoto Protocol.

little guidance exists today on how to calculate net reductions in CO_2 emissions through CCS project-based activities. An appropriate baseline scenario can minimise the risk that a project receives credits for avoiding emissions that would have been avoided also in the absence of the project (Haefeli et al., 2004).

9.3.2.2 Leakage in the context of the Kyoto mechanisms

The term 'Leakage' is defined according to Marrakesh Accord as "the net change of anthropogenic emissions by sources and/or removals by sinks of greenhouse gases which occurs outside the project boundary, and that is measurable and attributable to the Article 6 project". It has been proposed to use the term leakage for the emissions resulting from capture, transport and injection, which should not be confused with releases of CO_2 from a geological reservoir (escaped CO_2). According to Haefeli et al. (2004) current legislation does not deal with cross-border CCS projects and would need further clarification. Guidance would be especially needed to deal with cross-border projects involving CO_2 capture in an Annex I country that is party to the Kyoto Protocol and storage in a country that is not party to the Kyoto Protocol (or in an Annex I country that is not bound by the Kyoto Protocol).

Table 9.3 provides an overview of the different Kyoto mechanisms and the general principles and requirements of each (practical indices and specific accounting rules and procedures), for the purpose of developing within these mechanisms CCS accounting systems that can be employed for emissions control and reduction. Although the political process has not yet decided how CCS systems will be accepted under the different Kyoto mechanisms, these general procedures could be applicable to them as well as to other similar schemes on emission trading and projects.

9.4 Gaps in knowledge

Methodologies for incorporating CCS into national inventories and accounting schemes are under development. There are alternate ways for incorporating CCS (see Sections 9.2 and 9.3) and the data needs may be different depending on the choices made. The following gaps in knowledge and need for decisions to be made by the political process were identified:

- There is a lack of methodologies to estimate physical leakage from storage, as well as of emission factors (fugitive emissions) for estimating emissions from capture systems, and from transportation and injection processes.
- Geologic and ocean storage open new challenges regarding a) uuncertainty on the permanence of the stored emissions, b) the need for protocols on transboundary transport and storage, c) accounting rules for CCS and, d) insight on issues such as emission measurement, long term monitoring, timely detection and liability/responsibility
- There are no existing methodologies for reporting and verification of reduced emission under the Kyoto Mechanisms.
- Methods do not exist for estimating and dealing with potential emissions resulting from system failures, such as sudden geological faults and seismic activities or pipeline disruptions.

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Tables

Table 9.1. Potential sources and emissions of greenhouse gases (GHG) in the general phases of a CO_2 capture and storage system.

IPCC Guidelines			**Emissions**	**Capture**	**Transportation** (b)	**Injection**	Storage **(c)**
Sector (a)	**Source Category** (a)						
1 Energy	GHG Emissions from stationary combustion 1A1; 1A2		CO_2 CH_4, N_2O, NO_x, CO, NMVOCs, SO_2	●		●	
1 Energy	GHG Emissions from mobile combustion	Water-borne navigation 1A3di, (d) 1A3dii (e)	CO_2 CH_4, N_2O, NO_x, CO, NMVOCs, SO_2		●		
		Other transportation (pipeline transportation) 1A3ei	CO_2 CH_4, N_2O, NO_x, CO, NMVOCs, SO_2		●		
1 Energy	Fugitive emissions from fuels 1B	Oil and natural gas 1B2 (f)	CO_2; CH_4; N_2O NMVOCs	●		●	
2 Industrial Processes (does not include emissions from fuel combustion)	Mineral products 2A	(e.g., Cement)	CO_2, SO_2	●		●	
	Chemical industry 2B	(e.g., Ammonia)	CO_2, NMVOCs CO, SO_2	●		●	
	Metal production 2C	(e. g., Iron and Steel)	CO_2, NO_x, NMVOCs, CO, SO_2	●		●	
	Other production 2D	(e.g. Food and Drink)	CO_2, NMVOCs	●		●	
6 Waste	Industrial wastewater handling 6B1		CH_4	●			
	Fugitive CO_2 emissions from capture, transportation and injection processes (g)	Normal operations	CO_2	●	●	●	
		Repair and maintenance	CO_2	●	●	●	
		Systems upsets and accidental discharges	**CO_2**	●	●	●	

1- IPCC Source/sink category numbering (see also IPCC (1997), Vol.1, Common Reporting Framework).

2- Emissions from transportation include both GHG emissions from fossil fuel use and fugitive emissions of CO_2 from pipelines and other equipment/processes. Besides ships and pipelines limited quantities of CO_2 could be transported by means of railways or by trucks, source categories identified in the IPCC Guidelines/GPG2000.

3- The long-term physical leakage of stored CO_2 is not covered by the existing framework for the reporting of emissions in the *IPCC Guidelines*. Different potential options exist to report these emissions in the inventories (e.g., in the relevant sectors/categories producing the emissions, creating a separate and new category under fugitive emissions, creating a new category for the capture, transportation and/or storage industry etc.). No final conclusion can still be made on which reporting option is more appropriate taking into account the different variants adopted by the CCS systems.

4- International Marine (Bunkers). Emissions based upon fuel sold to ships engaged in international transport should not be included in national totals but reported separately under Memo Items.

5- National Navigation.

6- Emissions related to the capture (removal) of CO2 in natural gas processing installations to improve the heating valued of the gas or to meet pipeline specifications.

7- A general framework for estimation of fugitive emissions is included in the *IPCC Guidelines* in the Energy sector. However, estimation and reporting of fugitive emissions from CCS need further elaboration of the methodologies.

Table 9.2. Differences in the forms of carbon storage that might influence the way accounting is conducted.

Property	Terrestrial Biosphere	Deep Ocean	Geologic Reservoirs
CO_2 sequestered or stored	Stock changes can be monitored over time.	Injected carbon can be measured	Injected carbon can be measured
Ownership	Stocks will have a discrete location and can be associated with an identifiable owner.	Stocks will be mobile and may reside in international waters.	Stocks may reside in reservoirs that cross national or property boundaries and differ from surface boundaries.
Management decisions	Storage will be subject to continuing decisions about land-use priorities.	Once injected there are no further human decisions on maintenance.	Once injected human decisions to influence continued storage involve monitoring and perhaps some maintenance, unless storage interferes with resource recovery".
Monitoring	Changes in stocks can be monitored.	Changes in stocks will be modelled.	Release of CO2 might be detected by physical monitoring but the difficulty of monitoring over large areas may require modeling as well."
Time scale with expected high values for fraction CO_2 retained	Decades, depending on management decisions.	Centuries, depending on depth and location of injection.	Physical leakage from well-designed systems is expected to be very small, barring physical disruption of the reservoir.
Physical leakage	Losses might occur due to disturbance, climate change, or land-use decisions.	Losses will assuredly occur as an eventual consequence of marine circulation and equilibration with the atmosphere.	Losses are likely to be small for well-designed systems except in the case of physical disruption of the reservoir.
Liability	A discrete land-owner can be identified with the stock of sequestered carbon.	Multiple parties may contribute to the same stock of stored carbon and the carbon may reside in international waters.	Multiple parties may contribute to the same stock of stored carbon that may lie under multiple countries.

Table 9.3. Accounting issues related to Kyoto Mechanisms.

Mechanism	Article no.	Principle	Requirements in relation to CCS	Basic considerations
Joint implementation (JI)	Article 6.1 KP	As a general principle, any Annex I party may transfer to or obtain from another Annex I party Emission Reduction Units (ERUs) that shall result from projects that seek to reduce GHG emissions by sources and/or enhance removals by sinks.	• Set modalities and procedures to set the project in a transparent manner • Procedures for verification and certification of ERU.	Important to ensure that credits received from projects in Annex I countries result from emission reductions that are real and additional to what would have happened in the absence of the project i.e. are measured against baselines.
Clean Development Mechanism (CDM)	Article 12.2 KP	• Intended to promote sustainable develop-ment in developing countries through the allowance of trade between developed and developing countries. • Refers to the establishment of a CDM with the objective of assisting Annex I parties to achieve part of their Article 3 KP emission reduction commitments through the implementation of project-based activities generating emission cut/backs and/or enhanced sink removals.	Highly detailed set of modalities and procedures regarding issues such as: • project level versus national level obligations • modelled versus actual amounts of credits • timing of sequestration and liabilities in the long run.	• Overall baseline methodology • Annex I parties shall be able to acquire Certified Emission Reductions (CERs) from projects implemented in non Annex I countries. • Should provide real, measurable and long-term benefits related to the mitigation of climate change, i.e. will be measured against baselines.
Emission trading (ET)	Article 17 KP	Allows for trading between developed countries that have targets and assigned amount units (AAUs) allocated to them through the KP, it endorses the basic principle of the use of ET as a mean available to Annex I parties to achieve their emission commitment.	• Cap (emission trading) i.e. the maximum amount of allowable emission offsets between Annex I countries; • Net versus gross accounting (measures in non-Annex I).	• Trade is based on national Assigned Amounts (AAUs) to individual countries. • The proposed guidelines for ET contain provisions on the amount of AAUs that may be traded between Annex I parties so as to avoid overselling of quotas. It also contains several options that would impose a quantified upper limit on the amount of AAUs that a transferring party could trade. • A successful carbon trading system must accurately measure the offsets and credits to assure companies that

				they will receive the reductions.

Figures

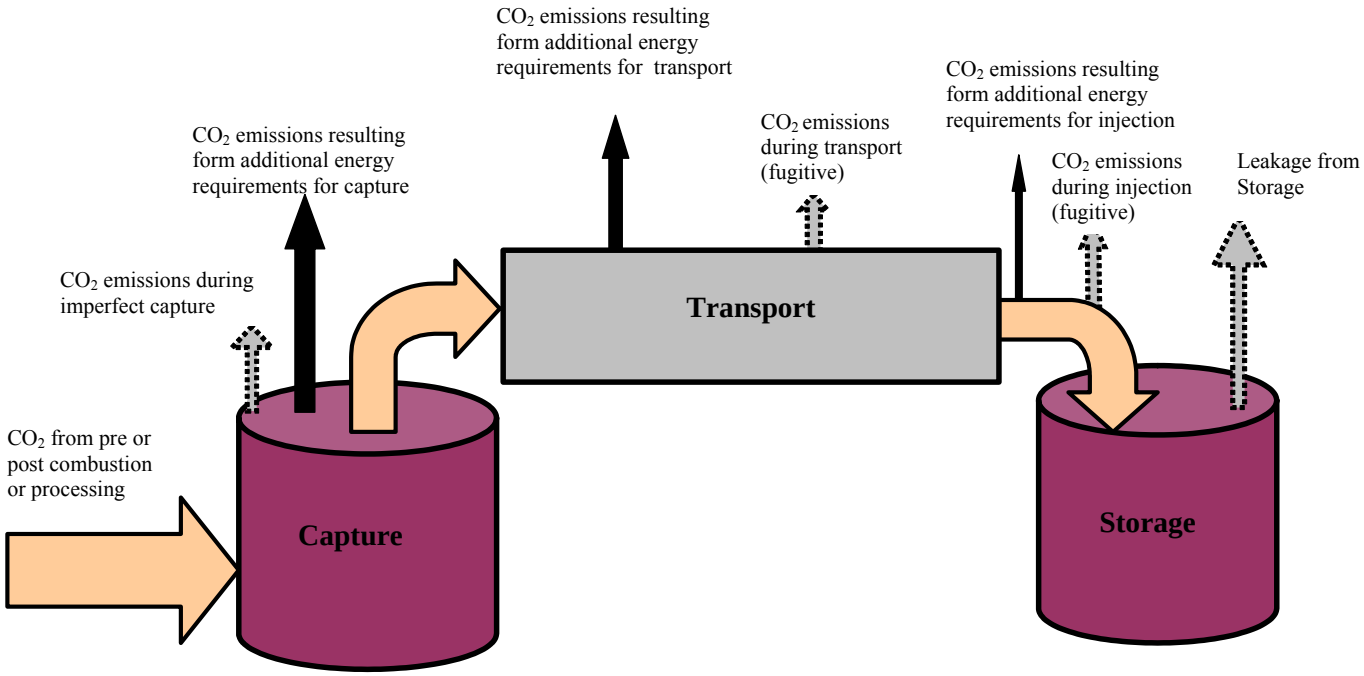

Figure 9.1. A simple flow diagram showing possible CO_2 emission sources during different phases of the CO_2 capture and storage chain.

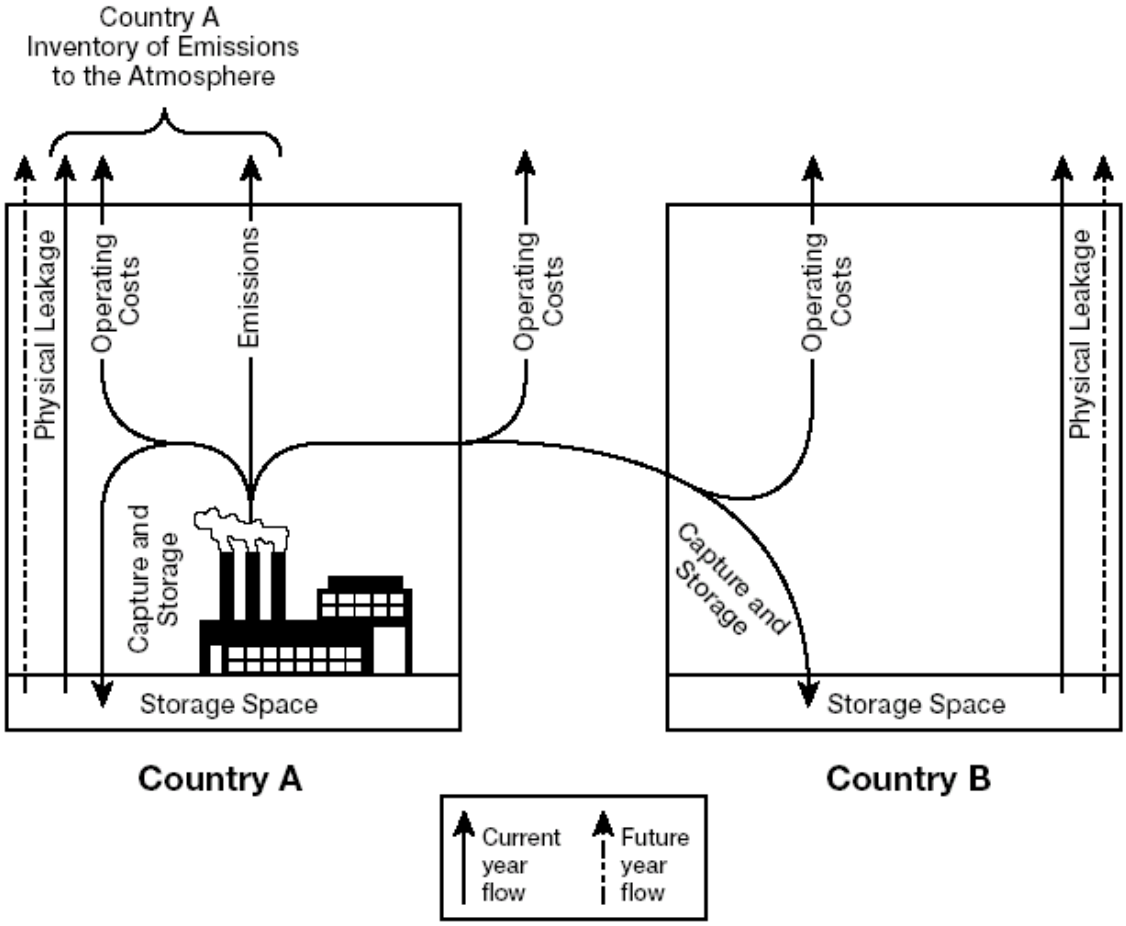

Figure 9.2. A simple flow diagram on how CO_2 capture and storage could transcend traditional accounting boundaries.[17]

[17] The operating costs shown are the CO_2 emitted as a result of the added energy required to operate the system plus fugitive emissions from separation, transport, and injection.

AI Properties of CO_2 and carbon-based fuels

Coordinating Lead Author
PAUL FREUND (UNITED KINGDOM)

Lead Authors
Stefan Bachu (Canada), Dale Simbeck (United States), Kelly (Kailai) Thambimuthu (Australia and Canada)

Contributing Author
Murlidhar Gupta (Canada and India)

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AI.1 Introduction to Appendix I

In this Appendix, data on relevant physical and chemical properties of CO_2 are presented, together with an outline of the health effects of CO_2, and a summary of some of the typical recommendations for avoiding harm to humans. Established uses for CO_2 are listed and some common conversion factors presented which are relevant to this report. An introduction is also provided to the main types of fossil fuels and other carbon-containing fuels as background to considering how their use produces CO_2.

AI.2 Carbon Dioxide

Carbon dioxide is a chemical compound consisting of two elements, carbon and oxygen, in the ratio of one to two; its molecular formula is CO_2. It plays a vital role in the earth's environment, being a necessary ingredient in the life cycle of animals and plants. Found in small proportions in the atmosphere (370 ppm), CO_2 is assimilated by plants which in turn produce oxygen. Anthropogenic activities which cause the emission of CO_2 include the combustion of fossil fuels and other carbon-containing materials, the fermentation of organic compounds such as sugar and the breathing of humans. Natural sources of CO_2, including volcanic activity, dominate the earth's carbon cycle.

CO_2 gas has a slightly irritating odour, is colourless and is denser than air. Although it is a normal, if minor, constituent of air, high concentrations of CO_2 can be dangerous.

AI.2.1 Physical properties of CO_2

AI.2.1.1 General

At normal temperature and pressure, carbon dioxide is a gas. The physical state of CO_2 varies with temperature and pressure as shown in Figure AI.1 - at low temperatures CO_2 is a solid; on warming, if the pressure is below 5.1 bar, the solid will sublime directly into the vapour state. At intermediate temperatures (between -56.5°C, the temperature of the triple point, and 31.1°C, the critical point), CO_2 may be turned from a vapour into a liquid by compressing it to the corresponding liquefaction pressure (and removing the heat produced).

Figure AI.1. Phase diagram for CO_2 (based on Shakhashiri).

At temperatures higher than 31.1°C (if the pressure is greater than 73.9 bar, the pressure at the critical point), CO_2 is said to be in a supercritical state where it behaves as a gas; indeed under high pressure, the density of the gas can be very large, approaching or even exceeding the density of liquid water (also see Figure AI.2). This is an important aspect of CO_2's behaviour, especially relevant for storage of CO_2.

Figure AI.2. Variation of CO_2 density as a function of temperature and pressure (Bachu, 2003).

Each of the phase changes across the solid-gas, solid-liquid and liquid-gas boundaries (see Figure AI.1) take-up or release heat (i.e. the relevant latent heat). On the other hand, the phase changes from supercritical condition to liquid or from supercritical to gas do not require or release heat. This property is useful for the design of CO_2 compression facilities since, if this can be exploited, it avoids the need to handle the heat associated with the liquid-gas phase change.

AI.2.1.2 Specific physical properties

There is a substantial body of scientific information available on the physical properties of CO_2. Selected physical properties of CO_2 are given in Table AI.1. The phase diagram for CO_2 is shown in Figure AI.1. The Equation of State for CO_2 has been investigated by many authors (see for example Span and Wagner, 1996). The variation of the density of CO_2 as a function of temperature and pressure is shown in Figure AI.2, the variation of vapour pressure of CO_2 with temperature in Figure AI.3, and the variation of viscosity with temperature and pressure in Figure AI.4. Further information on viscosity can be found in Fenghour *et al.* (1998). The pressure-enthalpy chart for CO_2 is shown in Figure AI.5. The solubility of CO_2 in water is described below.

Table AI.1. Physical properties of CO_2.

Figure AI.3. Vapour pressure of CO_2 as a function of temperature (Span and Wagner, 1996).

Figure AI.4. Variation of CO_2 viscosity as a function of temperature and pressure (Bachu, 2003).

Figure AI.5. Pressure-Enthalpy chart for CO_2.

Figure AI.6. Solubility of CO_2 in water (Kohl and Nielsen, 1997).

AI.2.2 Chemical properties of CO_2

AI.2.2.1 General

Some thermodynamic data for CO_2 and a few related compounds are given in Table AI.2

Table AI.2. Thermodynamic data for selected Carbon-containing compounds (ref. Cox et al., 1989 and other sources).

In an aqueous solution carbon dioxide forms carbonic acid, which is too unstable to be easily isolated. The solubility of CO_2 in water (Figure AI.6) decreases with increasing temperature and increases with increasing pressure. The solubility of CO_2 in water also decreases with increasing water salinity by as much as one order of magnitude (Figure AI.7). The following empirical relation (Enick and Klara, 1990) can be used to estimate CO_2 solubility in brackish water and brine:

$$w_{CO2,\,b} = w_{CO2,\,w} \cdot (1.0 - 4.893414 \cdot 10^{-2} \cdot S + 0.1302838 \cdot 10^{-2} \cdot S^2 - 0.1871199 \cdot 10^{-4} \cdot S^3)$$

where w_{CO2} is CO_2 solubility, S is water salinity (expressed as total dissolved solids in weight %), and the subscripts *w* and *b* stand for pure water and brine, respectively.

Figure AI.7. Solubility of CO_2 in brine relative to that in pure water, showing experimental points reported by Enick and Klara, 1990, and correlation developed by those authors. (TDS stands for total dissolved solids).

A solid hydrate separates from aqueous solutions of CO_2 that are chilled (below about 11 ^{o}C) at elevated pressures. A hydrate is a crystalline compound consisting of the host (water) plus guest molecules. The host is formed from a tetrahedral hydrogen-bonding network of water molecules; this network is sufficiently open to create pores (or cavities) that are large enough to contain a

variety of other small molecules (the guests). Guest molecules can include CH_4 and CO_2. CO_2 hydrates have similar (but not identical) properties to methane hydrates, which are extensively studied because of their effects on natural gas production, as well as because they may be future sources of hydrocarbons. CO_2 hydrates have not been studied as extensively.

AI.2.2.2 Impact of CO_2 on pH of water

The dissolution of CO_2 in water (this may be seawater, or the saline water in geological formations) involves a number of chemical reactions between gaseous and dissolved carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}) which can be indicated thus:

$$CO_{2(g)} = CO_{2\ (aq)}$$

$$CO_{2(aq)} + H_2O = H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} = H^+_{(aq)} + HCO^-_{3\ (aq)}$$

$$HCO^-_{3\ (aq)} = H^+_{(aq)} + CO^{2-}_{3\ (aq)}$$

Addition of CO_2 to water leads initially to an increase in the amount of dissolved CO_2. The dissolved CO_2 reacts with water to form carbonic acid. Carbonic acid dissociates to form bicarbonate ions, which can further dissociate into carbonate ions. The net effect of dissolving *anthropogenic* CO_2 in water is the removal of carbonate ions and production of bicarbonate ions, with a lowering in pH

Figure AI.8 shows the dependence of pH on the extent of CO_2 dissolved in seawater at temperatures of 0°C and 25°C based on theoretical calculations (IEA Greenhouse Gas R&D Programme, 2000) by iterative solution of the relationships (Horne, 1969) for the carbonic acid/bicarbonate/carbonate equilibria combined with activity coefficients for the bicarbonate and carbonate ions in seawater. The temperature dependence of the ionisation of water and the bicarbonate equilibria were also included in this calculation. This gives values for the pH of typical seawater of 7.8-8.1 at 25°C and 8.1-8.4 at 0°C. These values, which are strongly dependent on carbonate/bicarbonate buffering, are in line with typical data for seawater (Figure AI.8 shows 2 experimental data points reported by Nishikawa et al., 1992).

Figure AI.8. Dependence of pH on CO_2 concentration in seawater.

Figure AI.8 also shows that there is a small effect of temperature on the reduction in pH that results from dissolution of CO_2. A minor pressure dependence of water ionisation is also reported (Handbook of Chemistry and Physics, 2000). The effect on water ionisation of an increase in pressure from atmospheric to 250 bar (equivalent to 2500 m depth) is minor and about the same as would result from increasing temperature by about 2°C. The effect of pressure can therefore be ignored.

AI.2.3 Health and safety aspects of exposure to CO_2

As a normal constituent of the atmosphere, where it is present in low concentrations (currently 370 ppm), CO_2 is considered harmless. CO_2 is non-flammable.

As it is 1.5 times denser than air at normal temperature and pressure, there will be a tendency for any CO_2 leaking from pipework or storage to collect in hollows and other low-lying confined spaces which could create hazardous situations. The hazardous nature of the release of CO_2 is enhanced because the gas is colourless, tasteless and is generally considered odourless unless present in high concentrations.

When contained under pressure, escape of CO_2 can present serious hazards, for example asphyxiation, noise level (during pressure relief), frostbite, hydrates/ice plugs, and high pressures (Jarrell et al., 2002). The handling and processing of CO_2 must be taken into account in preparing a health, safety and environment plan for any facility handling CO_2.

AI.2.3.1 Effects of exposure to CO_2

At normal conditions, the atmospheric concentration of CO_2 is 0.037%, a non-toxic amount. Most people with normal cardiovascular, pulmonary-respiratory, and neurological functions can tolerate exposure of up to 0.5 to 1.5% CO_2 for one to several hours without harm.

Higher concentrations or exposures of longer duration are hazardous – either by reducing the concentration of oxygen in the air to below the 16% level required to sustain human life[1], or by entering the body, especially the bloodstream, and/or altering the amount of air taken in during breathing – such physiological effects can occur faster than the effects of displacement of oxygen, depending on the concentration of CO_2. This is reflected in, for example, the current U.S. occupational exposure standard of 0.5% for the maximum allowable concentration of CO_2 in air for eight hours continuous exposure; the maximum concentration to which operating personnel may be exposed for a short period of time is 3.0%.

The impact on humans of elevated CO_2 concentrations depends on the concentration and duration of exposure. At concentrations up to 1.5%, there are no noticeable physical consequences for healthy adults at rest from exposure for an hour or more (Figure AI.9); indeed, exposure to slightly elevated concentrations of CO_2, such as in re-breathing masks on aeroplanes at high altitude, may produce beneficial effects (Benson et al., 2002). Increased activity or temperature may affect how the exposure is perceived. Longer exposure, even to less than 1% concentration, may significantly affect health. Noticeable effects occur above this level, particularly changes in respiration and blood pH level that can lead to increased heart rate, discomfort, nausea, and unconsciousness.

Figure AI.9. Effects of CO_2 exposure on humans (Fleming *et al.*, 1992).

It is noted (Rice, 2004) that most studies of the effects of CO_2 have involved healthy young male subjects, especially in controlled atmospheres such as submarines. Carbon dioxide tolerance in susceptible subgroups, such as children, the elderly, or people with respiratory deficiency, has not been studied to such an extent.

Acute exposure to CO_2 concentrations at or above 3% may significantly affect the health of the general population. Hearing loss and visual disturbances occur above 3% CO_2. Healthy young adults exposed to more than 3% CO_2 during exercise experience adverse symptoms, including laboured breathing, headache, impaired vision, and mental confusion. CO_2 acts as an asphyxiant in

[1] Signs of asphyxia will be noted when atmospheric oxygen concentration falls below 16%. Unconsciousness, leading to death, will occur when the atmospheric oxygen concentration is reduced to ≤ 8% although, if strenuous exertion is being undertaken, this can occur at higher oxygen concentrations (Rice, 2004).

the range 7-10% and can be fatal at this concentration; at concentrations above 20%, death can occur in 20 to 30 minutes (Fleming et al., 1992). The effects of CO_2 exposure are summarised in Table AI.3 which shows the consequences at different concentrations.

Table AI.3. Some reports of reactions to exposure to elevated concentrations of CO_2.

Health risks to the population could therefore occur if a release of CO_2 were to produce:
- relatively low ambient concentrations of CO_2 for prolonged periods,
- or intermediate concentrations of CO_2 in relatively anoxic environments,
- or high concentrations of CO_2.

The identification of CO_2 intoxication is done by exclusion of other causes because exposure to CO_2 does not produce unique symptoms.

AI.2.3.2 Occupational standards

Protective standards have been developed for workers who may be exposed to CO_2 (Table AI.4 shows US standards but similar standards are understood to apply in other countries). These standards may or may not be relevant for protection of the population at large against exposure to CO_2. Nevertheless, the occupational standards exist and provide a measure of the recommended exposure levels for this class of individual.

Table AI.4. Occupational Exposure Standards.

Site specific risk assessments using these and other health data are necessary to determine potential health risks for the general population or for more sensitive subjects.

AI.2.3.3 Sensitive Populations

Rice (2004) has indicated that there may be certain specific groups in the population which would be more sensitive than the general population to elevated CO_2 levels. Such groups include those suffering from certain medical conditions, including cerebral disease as well as patients in trauma, medicated patients, and those experiencing panic disorder, as well as individuals with pulmonary disease resulting in acidosis, children and people engaged in complex tasks.

CO_2 is a potent cerebro-vascular dilator, increasing cerebral blood flow significantly. CO_2 exposure can seriously compromise patients in coma or with head injury, increased intracranial pressure or bleeding, or expanding lesions. Elevation of partial pressure of CO_2 in arterial blood can further dilate cerebral vessels already dilated by anoxia.

The stimulation of the respiratory centre by CO_2 is depressed by anoxia and by various drugs (Osol and Pratt, 1973). In such patients, as well as patients with trauma to the head, the normal compensatory mechanisms would not protect them from exposure to CO_2 nor would their symptoms necessarily alert the individual or their carers to the presence of high CO_2 levels.

Patients susceptible to panic disorder may experience an increased frequency of panic attacks at 5% CO_2 (Woods et al., 1988). Panic attack and significant anxiety can affect the ability of the individual to exercise appropriate judgment in dangerous situations.

CO_2 exposure can increase pulmonary pressure as well as systemic blood pressure and should be avoided in individuals with systemic or pulmonary hypertension. The rise in cardiac work during CO_2 inhalation could put patients with coronary artery disease or heart failure in jeopardy (Cooper et al., 1970).

Infants and children breathe more air than adults relative to their body size and thus they tend to be more susceptible to respiratory exposures (Snodgrass, 1992). At moderate to high CO_2 concentrations, the relaxation of blood vessels and enhanced ventilation could contribute to rapid loss of body heat in humans of any age. CO_2 can significantly diminish an individual's performance in carrying out complex tasks.

AI.2.3.4 CO_2 control and response procedures

Suitable control procedures have been developed by the industries which use CO_2. For example, these would minimise any venting of CO_2 unless this cannot be avoided for safety or other operational reasons. Adequate ventilation must be provided when CO_2 is discharged into the air to ensure rapid dispersion.

Because of its high density, released CO_2 will flow to low levels and collect there, especially under stagnant conditions. High concentrations can persist in open pits, tanks and buildings. For this reason, monitors should be installed in areas where CO_2 might concentrate, supplemented by portable monitors. If CO_2 escapes from a vessel, the consequent pressure drop can cause a hazardous cold condition with danger of frostbite from contact with cold surfaces, with solid CO_2 (dry ice) or with escaping liquid CO_2. Personnel should avoid entering a CO_2 vapour cloud not only because of the high concentration of CO_2 but also because of the danger of frostbite.

Hydrates, or ice plugs, can form in the piping of CO_2 facilities and flowlines, especially at pipe bends, depressions, and locations downstream of restriction devices. It is not necessary for the temperatures to fall below zero for hydrates to form; this can occur at elevated pressures at up 11^{o}C.

AI.2.4 Established uses for CO_2

A long established part of the industrial gases market involves the supply of CO_2 to a range of industrial users (source: Air Liquide). In several major industrial processes, CO_2 is manufactured on site as an intermediate material in the production of chemicals. Large quantities of CO_2 are used for Enhanced Oil Recovery. Other uses of CO_2 include:

- Chemicals
  - Carbon dioxide is used in synthesis chemistry and to control reactor temperatures. CO_2 is also employed to neutralize alkaline effluents.
  - The main industrial use of CO_2 is in the manufacture of urea, as a fertiliser.
  - Large amounts of CO_2 are also used in the manufacture of inorganic carbonates and a lesser amount is used in the production of organic monomers and polycarbonates.
  - Methanol is manufactured using a chemical process which makes use of CO_2 in combination with other feedstocks
  - CO_2 is also used in the manufacture of polyurethanes
- Pharmaceuticals
  - CO_2 is used to provide an inert atmosphere, for chemical synthesis, supercritical fluid extraction and for acidification of wastewater and for product transportation at low temperature (-78oC).
- Food and Beverage

  - CO_2 is used in the food business in 3 main areas: carbonation of beverages; packaging of foodstuffs and as cryogenic fluid in chilling or freezing operations or as dry ice for temperature control during the distribution of foodstuffs.
- Healthcare
  - Intra-abdominal insufflation during medical procedures to expand the space around organs or tissues for better visualization.
- Metals industry
  - CO_2 is typically used for environment protection; for example for red fume suppression during scrap and carbon charging of furnaces, for nitrogen pick-up reduction during tapping of electric arc furnaces and for bottom stirring.
  - In non-ferrous metallurgy, carbon dioxide is used for fume suppression during ladle transfer of matte (Cu/Ni production) or bullion (Zn/Pb production).
  - A small amount of liquid CO_2 is used in recycling of waters from acid mine drainage.
- Pulp and paper
  - Carbon dioxide enables fine tuning of the pH of recycled mechanical or chemical pulps after an alkaline bleaching. CO_2 can be used for increasing the performance of paper production machines.
- Electronics
  - CO_2 is used in waste water treatment, and as a cooling medium in environmental testing of electronic devices. CO_2 can also be used to add conductivity to ultra-pure water and, as CO_2 snow, for abrasive cleaning of parts or residues on wafers; CO_2 can also be used as a supercritical fluid for removing photoresist from wafers, thus avoiding use of organic solvents.
- Waste treatment
  - Injection of CO_2 helps control the pH of liquid effluents.
- Other applications
  - CO_2 snow is used for fire extinguishers, for pH control and for regulation of waste waters in swimming pools.

AI.3 Conversion factors

Some conversion factors relevant to CO_2 capture and storage are given in Table AI.5. Other, less precise conversions and some approximate equivalents are given in Table AI.6.

AI.4 Fuels and emissions

AI.4.1 Carbonaceous fuels

Carbonaceous fuels can be defined as materials rich in carbon and capable of producing energy on oxidation. Looked at from a historical perspective, most of these fuels can be considered as carriers of solar energy, having been derived from plants which depended on solar energy for growth. Thus, these fuels can be distinguished by the time taken for their formation i.e. millions of years for fossil fuels, hundreds of years for peat and months-to-years for biofuels. On the scale of the human life span, fossil fuels are regarded as non-renewable carbonaceous fuels while biofuels are regarded as renewable. Coal, oil, and natural gas are the major fossil fuels. Wood, agro-wastes, etc. are the main biofuels for stationary uses but, in some parts of the world, crops such as soya, sugar cane and oil-seed plants are grown specifically to produce biofuels, especially transport fuels such as bioethanol and biodiesel. Peat is close to being a biofuel in terms of its relatively short formation time compared with fossil fuels.

AI.4.1.1 Coal

Coal is the most abundant fossil fuel present on earth. Coal originated from the arrested decay of the remains of plant life which flourished in swamps and bogs many millions of years ago in a humid, tropical climate with abundant rainfall. Subsequent action of heat and pressure and other physical phenomena metamorphosed it into coal. Because of various degrees of metamorphic change during the process, coal is not a uniform substance; no two coals are the same in every respect. The composition of coal is reported in two different ways: the proximate analysis and the ultimate analysis, both expressed in weight %. In a proximate analysis, moisture, volatile matter, fixed carbon, and ash are measured using prescribed methods, which enable the equipment designer to determine how much air is to be supplied for efficient combustion, amongst other things. An ultimate analysis determines the composition in terms of the elements that contribute to the heating value, such as carbon, hydrogen, nitrogen, sulphur, the oxygen content (by difference), as well as ash. Along with these analyses, the heating value (expressed as kJ/kg) is also determined.

Carpenter (1988) describes the various coal classification systems in use today. In general, these systems are based on hierarchy and rank. The rank of a coal is the stage the coal has reached during the coalification[2] process – i.e. its degree of metamorphism or maturity. Table AI.7 shows the classification system adopted by the American Society for Testing Materials (ASTM), D388-92A (Carpenter, 1988; Perry and Green, 1997). This rank-based system is extensively used in North America and many other parts of the world. This system uses two parameters to classify coals by rank, fixed carbon (dry, mineral-matter-free) for the higher rank coals and gross calorific value (moist, mineral-matter-free) for the lower rank coals. The agglomerating character of the coals is used to differentiate between adjacent coal groups.

AI.4.1.2 Oil and petroleum fuels

During the past 600 million years, the remains of incompletely decayed plant have become buried under thick layers of rock and, under high pressure and temperature, have been converted to petroleum which may occur in gaseous, liquid or solid form. The fluid produced from petroleum reservoirs may be crude oil (a mixture of light and heavy hydrocarbons and bitumen) or natural gas liquids. Hydrocarbons can also be extracted from tar sands or oil shales; this takes place in several parts of the world.

Fuels are extracted from crude oil through fractional distillation, with subsequent conversion and upgrading. Such fuels are used for vehicles (gasoline, jet fuel, diesel fuel and liquefied petroleum gases (LPG)), heating oils, lighting oils, solvents, lubricants, and building materials such as asphalts, plus a variety of other products. The compositions of heating fuels may differ in their composition, density, etc. but general categories are recognized worldwide: kerosene-type vaporizing fuel, distillate (or "gas oil"), and more viscous blends and residuals. Tables AI.8 and AI.9 provide typical specifications of some common fuels (Perry and Green, 1997; Kaantee et al., 2003).

AI.4.1.3 Natural Gas

Natural gas is combustible gas that occurs in porous rock of the earth's crust; it is often found with or near accumulations of crude oil. It may occur in separate reservoirs but, more commonly, it forms a gas cap entrapped between the petroleum and an impervious, capping rock layer in a

[2] Qalification refers to the progressive transformation of peat through lignite/brown coal, to sub-bituminous, bituminous and anthracite coals.

petroleum reservoir. Under high-pressure conditions, it becomes partially mixed with or dissolved in the crude oil. Methane (CH_4) is the main component of natural gas, usually making up greater than 80% of the constituents by volume. The remaining constituents are ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), hydrogen sulphide (H_2S), and inerts (N_2, CO_2, and He). The amounts of these compounds can vary greatly depending on location. Natural gas is always treated prior to use, mainly by drying, removing H_2S and, depending on the amount present, removal of CO_2. There are no universally accepted specification systems for marketed natural gas; however a typical composition of natural gas is given in Table AI.10 (Spath and Mann, 2000).

AI.4.1.4 Biofuels

Biofuels may be defined as fuels produced from organic matter or combustible oils produced by plants (IPCC, 2001). Dedicated energy crops, including short-rotation woody crops such as hardwood trees and herbaceous crops such as switch grass, are agricultural crops that are solely grown for use as biofuels. These crops have very fast growth rates and so can provide a regular supply of fuel. The category of biofuels also includes wood from trees and wood waste products (e.g. sawdust, wood-chips, etc.), crop residues (e.g. rice husks, bagasse, corn husks, wheat chaff, etc.). This category of fuel is often taken as including some types of municipal, animal and industrial wastes (e.g. sewage sludge, manure, etc.). These would be combusted in stationary plants. Chemical properties of typical biofuels, including peat, are given in Table AI.11 (Sami et al., 2001; Hower, 2003).

Biomass derived-fuels can also be manufactured for use as transport fuels, for example ethanol from fermentation of plant material or bio-diesel produced by trans-esterification of vegetable oils. The energy efficiency of fermentation systems can be improved by combustion of the solid residues to produce electricity.

AI.4.2 Examples of emissions from carbonaceous fuels

Depending on the fuel type and application, the utilisation of carbonaceous fuels causes direct and indirect emissions of one or more of the following: SO_x, NO_x, particulate matter, trace metals and elements, volatile organic carbons and greenhouse gases (e.g. CO_2, CH_4, N_2O). Direct emissions are usually confined to the point of combustion of the fuel. Indirect emissions include those that arise from the upstream recovery, processing and distribution of the fuel. Life cycle analysis (LCA) can be used to account for all emissions (direct as well as indirect) arising from the recovery, processing, distribution and end use of a fuel. Table AI.12 (Cameron, 2002) and Table AI.13 (EPA, 2004) give an idea of some direct and indirect emissions anticipated but these should be regarded only as examples as there can be considerable variation in many of these values.

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Tables

Table AI.1. Physical properties of CO_2.

Property	Value
Molecular weight	44.01
Critical temperature	31.1°C
Critical pressure	73.9 bar
Critical density	467 kg/m^3
Triple point temperature	-56.5 °C
Triple point pressure	5.18 bar
Boiling (sublimation) point (1.013 bar)	-78.5 °C
Gas phase	
Gas density (1.013 bar at boiling point)	2.814 kg/m^3
Gas density (@ STP)	1.976 kg/m^3
Specific volume (@ STP)	0.506 m^3/kg
C_p (@ STP)	0.0364 kJ/(mol.K)
C_v (@ STP)	0.0278 kJ/(mol.K)
C_p/C_v (@ STP)	1.308
Viscosity (@ STP)	13.72 μN.s/m^2 (or μPa.s)
Thermal conductivity (@ STP)	14.65 mW/(m.K)
Solubility in water (@ STP)	1.716 vol/vol
Enthalpy (@ STP)	21.34 kJ/mol
Entropy (@ STP)	117.2 J/mol.K
Entropy of formation	213.8 J/mol.K
Liquid phase	
Vapour pressure (at 20 °C)	58.5 bar
Liquid density (at -20 °C and 19.7 bar)	1032 kg/m^3
Viscosity (@ STP)	99 μN.s/m^2 (or μPa.s)
Solid phase	
Density of carbon dioxide snow at freezing point	1562 kg/m^3
Latent heat of vaporisation (1.013 bar at sublimation point)	571.1 kJ/kg

where STP stands for Standard Temperature and Pressure, which is 0 °C and 1.013 bar
Sources: Air Liquide gas data table; Kirk-Othmer (1985); NIST (2003).

Table AI.2. Thermodynamic data for selected Carbon-containing compounds (ref. Cox et al., 1989 and other sources).

Compound	Heat of formation $\Delta H_f°$ kJ mol^{-1}	Gibbs free energy of formation $\Delta G_f°$ kJ mol^{-1}	Entropy of formation $S_f°$ J mol^{-1} K^{-1}
CO (g)	-110.53	-137.2	197.66
CO_2 (g)	-393.51	-394.4	213.78
CO_2 (l)		-386	
CO_2 (aq)	-413.26		119.36
CO_3^{2-} (aq)	-675.23		-50.0
CaO (s)	-634.92		38.1
HCO_3^- (aq)	-689.93	-603.3	98.4
H_2O (l)	-285.83		69.95
H_2O (g)	-241.83		188.84
$CaCO_3$ (s)	-1207.6 (calcite)	-1129.1	91.7
	-1207.8 (aragonite)	-1128.2	88
$MgCO_3$ (s)	-1113.28 (magnesite)	-1029.48	65.09
CH_4 (g)	-74.4	-50.3	186.3
CH_3OH (l)	-239.1	-166.6	126.8
(g)	-201.5	-162.6	239.8

Table AI.3. Some reports of reactions to exposure to elevated concentrations of CO_2.

CO_2	Exposure Reactions	
Concentrn.	**Air Products (2003)**	**Rice (2004)**
1%	Slight increase in breathing rate.	Respiratory rate increased by ~ 37%
2%	Breathing rate increases to 50% above normal level. Prolonged exposure can cause headache, tiredness.	Ventilation rate raised by ~l00%. Respiratory rate raised by ~50%; Increased brain blood flow.
3%	Breathing increases to twice normal rate and becomes laboured. Weak narcotic effect. Impaired hearing, headache, increase in blood pressure and pulse rate.	Exercise tolerance reduced in workers when breathing against inspiratory & expiratory resistance.
4-5%	Breathing increases to approximately four times normal rate; symptoms of intoxication become evident and slight choking may be felt.	Increase in ventilation rate by ~200%; Respiratory rate doubled, dizziness, headache, confusion, dyspnea.
5-10%	Characteristic sharp odour noticeable. Very laboured breathing, headache, visual impairment, and ringing in the ears. Judgment may be impaired, followed within minutes by loss of consciousness.	At 8-10%, severe headache, dizziness, confusion, dyspnea, sweating, dim vision At 10%, unbearable dyspnea, followed by vomiting, disorientation, hypertension, & loss of consciousness.
50-100%	Unconsciousness occurs more rapidly above 10% level. Prolonged exposure to high concentrations may eventually result in death from asphyxiation.	

Table AI.4. Occupational Exposure Standards.

	Time Weighted Average (8 hour day/ 40 hour week)	Short Term Exposure Limit (15 minute)	Immediately Dangerous to Life and Health
Permissible Exposure Limit[a]	5 000 ppm (0.5%)		
Recommended Exposure Limit[b]	5 000 ppm (0.5%)	30 000 ppm (3%)	40 000 ppm (5%)
Threshold Limit Value[c]	5 000 ppm (0.5%)		

[a] OSHA US Occupational Safety and Health Administration
[b] NIOSH US National Institute of Occupational Safety and Health (1997)
[c] ACGIH American Conference of Governmental Industrial Hygienists.

Table AI.5. Some conversion factors.

To convert:	Into the following units:	Multiply by:
US gallon	Litre	3.78541
Barrels (bbl)	m^3	0.158987
ton (Imperial)	Tonne	1.01605
Short ton (US)	tonne	0.907185
lbf	N	4.44822
kgf	N	9.80665
lbf/in^2	Bar	0.0689476
Bar	MPa	0.1
Btu	MJ	0.00105506
Btu	kWh	0.000293071
kWh	MJ	3.60000
Btu/lb	MJ/kg	0.00232600
Btu/ft^3	MJ/m^3	0.0372589
Btu/h	kW	0.000293071
$Btu/(lb.^oF)$	$kJ/(kg.^oC)$	4.18680
$Btu/(ft^2.h)$	kW/m^2	0.00315459
$Btu/(ft^3.h)$	kW/m^3	0.0103497
$Btu/(ft^2.h.^oF)$	$W/(m^2.^oC)$	5.67826
1 MMT*	million tonnes	0.907185
^oF	^oC	$^oC = \frac{(^oF - 32)}{1.8}$

* The abbreviation MMT is used in the literature to denote both Millions of short tons and Millions of metric tonnes. The conversion given here is for the former.

Table AI.6. Approximate equivalents and other definitions.

To convert	Into the following units	Multiply by
1 t C	t CO_2	3.667
1 t CO_2	m^3 CO_2 (at 1.013 bar and 15 ^oC)	534
1 t crude oil	Bbl	7.33
1 t crude oil	m^3	1.165
Other definitions		
Standard Temperature and Pressure	0 ^oC and 1.013 bar	

Table AI.7. Characterization of coals by rank (according to ASTM D388-92A).

	Fixed Carbon limits (dmmf basis)[#] %		Volatile Matter limits (dmmf basis)[#] %		Gross Calorific Value limits (mmmf basis)[†] MJ/kg		
Class group	**Equal to or greater than**	**Less than**	**Greater than**	**Equal to or less than**	**Equal to or greater than**	**Less than**	**Agglomerating character**
Anthracite							
Meta-anthracite	98	-	-	2	-	-	Non-agglomerating
Anthracite	92	98	2	8	-	-	
Semi-anthracite [††]	86	92	8	14	-	-	
Bituminous coal							
Low volatile	78	86	14	22	-	-	
Medium volatile	69	78	22	31	-	-	Commonly agglomerating
High volatile A	-	69	31	-	32.6[‡]	-	
High volatile B	-	-	-	-	30.2[‡]	32.6	
High volatile C	-	-	-	-	26.7	30.2	
					24.4	26.7	Agglomerating
Sub-bituminous coal							
A	-	-	-	-	24.4	26.7	Non-agglomerating
B	-	-	-	-	22.1	24.4	
C	-	-	-	-	19.3	22.1	
Lignite							
A	-	-	-	-	14.7	19.3	
B	-	-	-	-	-	14.7	

[†] mmmf indicates moist mineral-matter-free basis; moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal. [#] indicates dry-mineral-matter-free basis (dmmf). [††] If agglomerating, classified in the low volatile group of the bituminous class

‡ Coals having 69% or more fixed carbon (dmmf) are classified according to fixed carbon, regardless of gross calorific value.

Table AI.8. Typical specifications of petroleum-based heating fuels.

Specifier	Number	Category
Canadian Government Specification Board, Department of Defense Production, Canada	3-GP-2	Fuel oil, heating
Deutsches Institut fur Normung e.V., Germany	DIN 51603	Heating (fuel) oils
British Standards Institution, UK	B.S. 2869	Petroleum fuels for oil engines and burners
Japan	JIS K2203	Kerosene
	JIS K2204	Gas oil
	JIS K2205	Fuel oil
Federal Specifications, United States	ASTM D 396	Fuel oil, burner

Table AI.9. Typical ultimate analysis of petroleum-based heating fuels.

Composition %	No. 1 fuel oil (41.5° A.P.I. †)	No. 2 fuel oil (33° A.P.I. †)	No. 4 fuel oil (23.2° A.P.I. †)	Low sulphur, No. 6 fuel oil (33° A.P.I. †)	High sulphur, No. 6 fuel oil (15.5° A.P.I. †)	Petroleum coke††
Carbon	86.4	87.3	86.47	87.26	84.67	89.5
Hydrogen	13.6	12.6	11.65	10.49	11.02	3.08
Oxygen	0.01	0.04	0.27	0.64	0.38	1.11
Nitrogen	0.003	0.006	0.24	0.28	0.18	1.71
Sulphur	0.09	0.22	1.35	0.84	3.97	4.00
Ash	<0.01	<0.01	0.02	0.04	0.02	0.50
C/H Ratio	6.35	6.93	7.42	8.31	7.62	29.05

† Degree API = (141.5/s) –131.5; where s is the specific density at 15°C; †† reference: Kaantee et al., 2003.

Table AI.10. Typical Natural Gas Composition.

Component	Pipeline composition used in analysis	Typical range of wellhead components (mol%)	
	Mol% (dry)	Low value	High value
Carbon dioxide CO_2	0.5	0	10
Nitrogen N_2	1.1	0	15
Methane CH_4	94.4	75	99
Ethane C_2H_6	3.1	1	15
Propane C_3H_8	0.5	1	10
Iso-butane C_4H_{10}	0.1	0	1
N-butane C_4H_{10}	0.1	0	2
Pentanes + (C_5^+)	0.2	0	1
Hydrogen Sulphide (H_2S)	0.0004	0	30
Helium (He)	0.0	0	5
Heat of combustion (LHV)	48.252 MJ/kg	-	-
Heat of combustion (HHV)	53.463 MJ/kg	-	-

Table AI.11. Chemical Analysis and Properties of some biomass fuels (Sami *et al.*, 2001; Hower, 2003).

	Peat	**Wood (saw dust)**	**Crop residues (sugarcane bagasse)**	**Municipal solid waste**	**Energy crops (Eucalyptus)**
Proximate Analysis					
Moisture	70-90	7.3	-	16-38	-
Ash	-	2.6	11.3	11-20	0.52
Volatile matter	45-75	76.2	-	67-78	-
Fixed carbon	-	13.9	14.9	6-12	16.9
Ultimate analysis					
C	45-60	46.9	44.8	-	48.3
H	3.5-6.8	5.2	5.4	-	5.9
O	20-45	37.8	39.5	-	45.1
N	0.75-3	0.1	0.4	-	0.2
S	-	0.04	0.01	-	0.01
Heating value, MJ/kg, (HHV)	17-22	18.1	17.3	15.9-17.5	19.3

Table AI.12. Direct emissions of non-greenhouse gases from two examples of coal and natural gas plants based on best available control technology, burning specific fuels (Cameron, 2002).

Emissions	Coal (supercritical PC with best available emission controls)	Natural Gas (NGCC with SCR)
NO_x, g/GJ	4-5	5
SOx, g/GJ	4.5-5	0.7
Particulates, g/GJ	2.4-2.8	2
Mercury, mg/GJ	0.3-0.5	N/A

Table AI.13. Direct CO_2 emission factors for some examples of carbonaceous fuels.

Carbonaceous Fuel	Heat content (HHV) MJ/kg††	Emission Factor g CO_2/MJ††
Coal		
Anthracite	26.2	96.8
Bituminous	27.8	87.3
Sub-bituminous	19.9	90.3
Lignite	14.9	91.6
Biofuel		
Wood (dry)	20.0	78.4
Natural Gas	**kJ/m^3**	
	37.3	50
Petroleum Fuel	**MJ/m^3**	
Distillate Fuel Oil (#1, 2 &4)	38650	68.6
Residual Fuel Oil (#5 & 6)	41716	73.9
Kerosene	37622	67.8
LPG (average for fuel use	25220	59.1
Motor gasoline	**-**	**69.3**

†† Reported values converted to SI units (NIES, 2003).

Figures

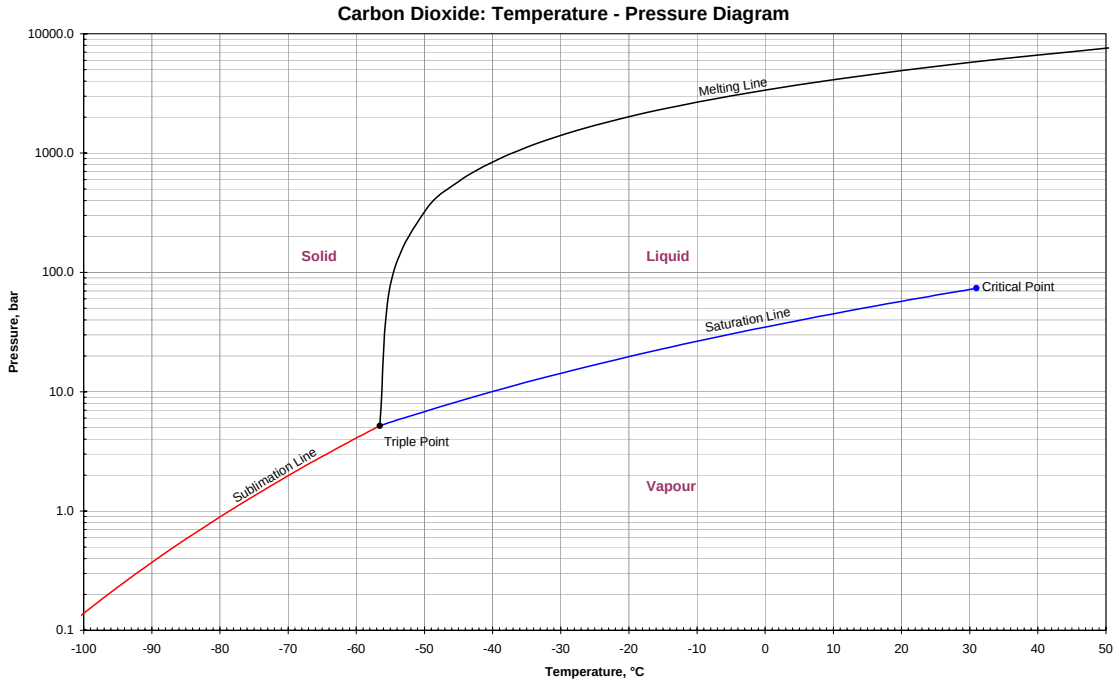

Figure AI.1. Phase diagram for CO_2 (based on Shakhashiri).
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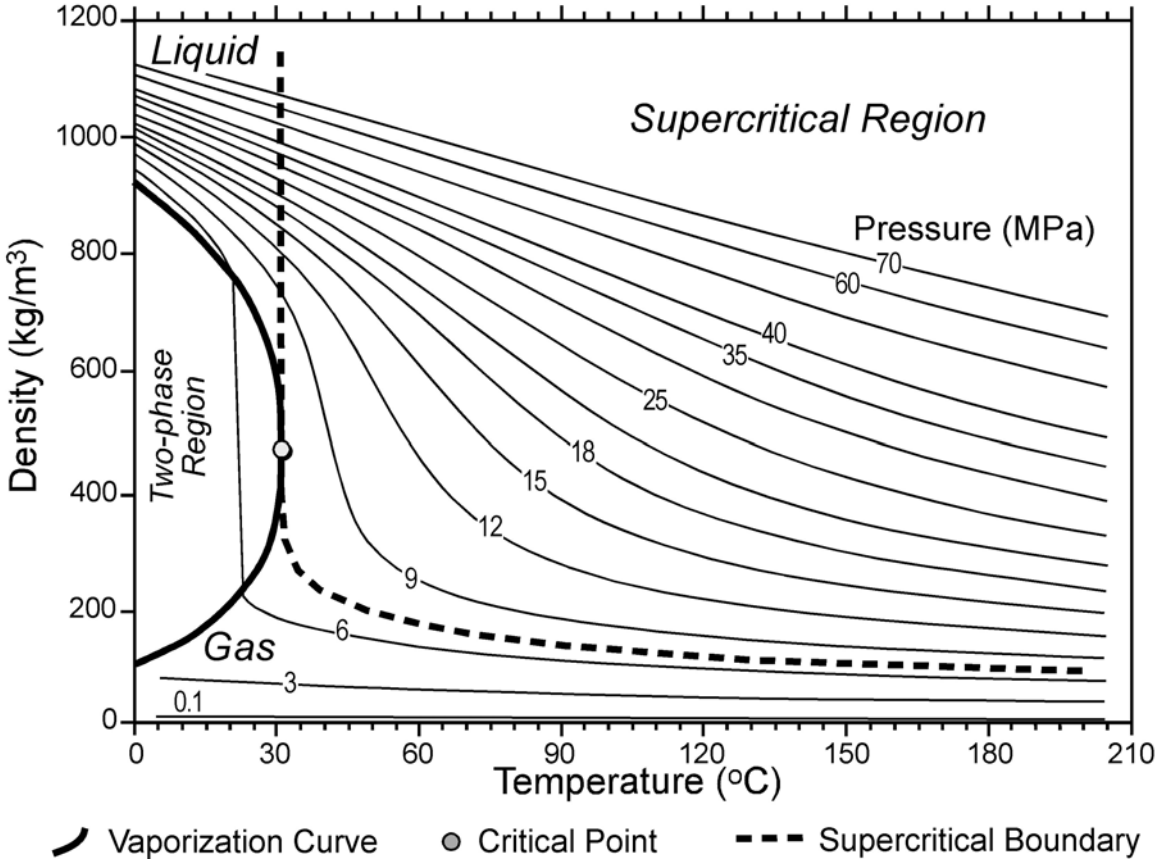

Figure AI.2. Variation of CO_2 density as a function of temperature and pressure (Bachu, 2003).

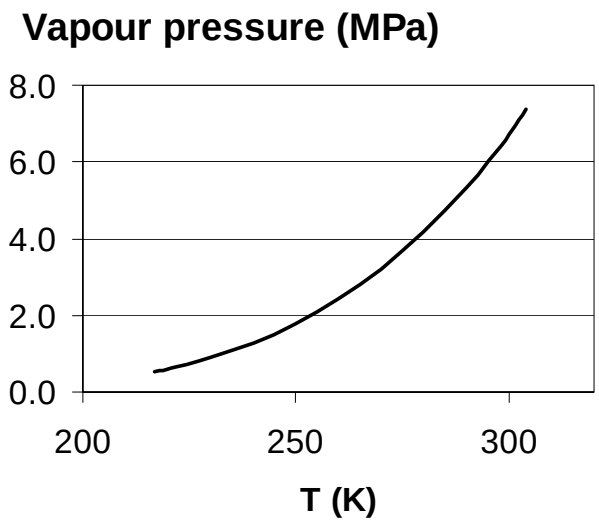

Figure AI.3. Vapour pressure of CO_2 as a function of temperature (Span and Wagner, 1996).

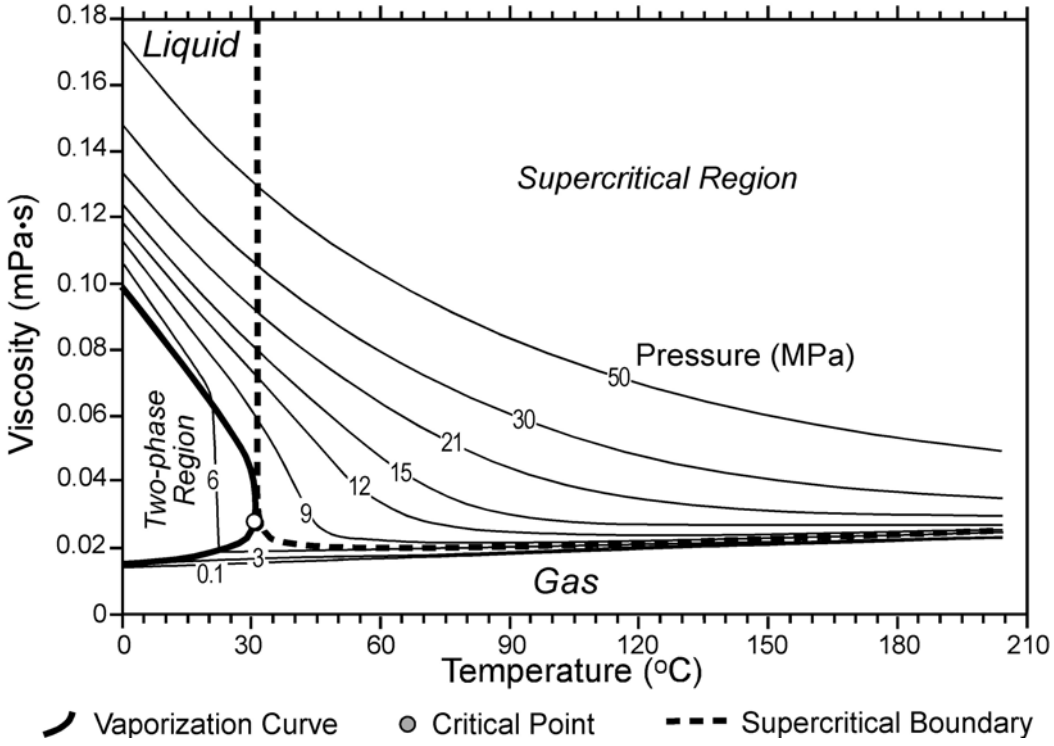

Figure AI.4. Variation of CO_2 viscosity as a function of temperature and pressure (Bachu, 2003).

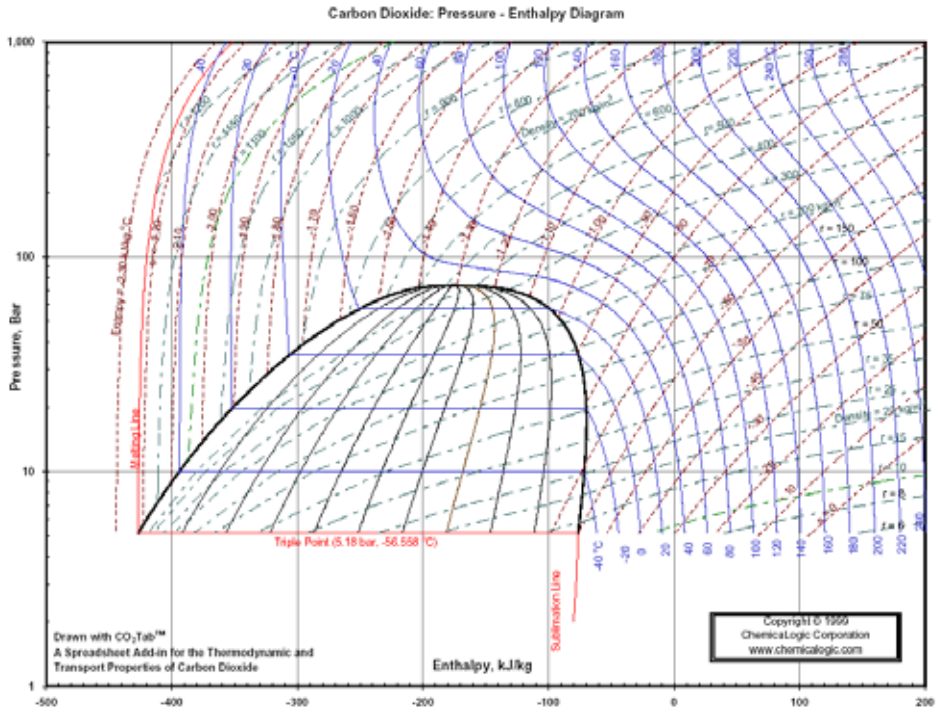

Figure AI.5. Pressure-Enthalpy chart for CO_2.

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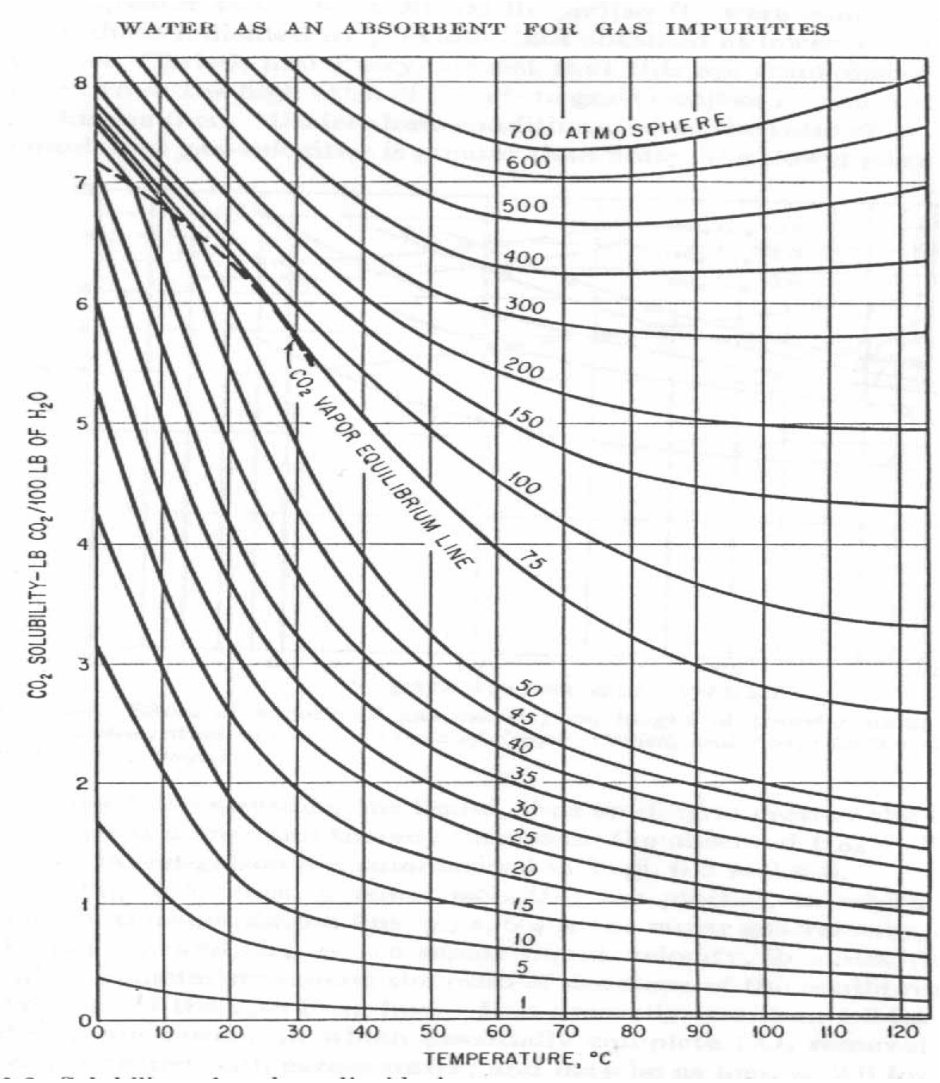

Figure AI.6. Solubility of CO_2 in water (Kohl and Nielsen, 1997).
NB: This graph must be re-drawn in SI units before publication.

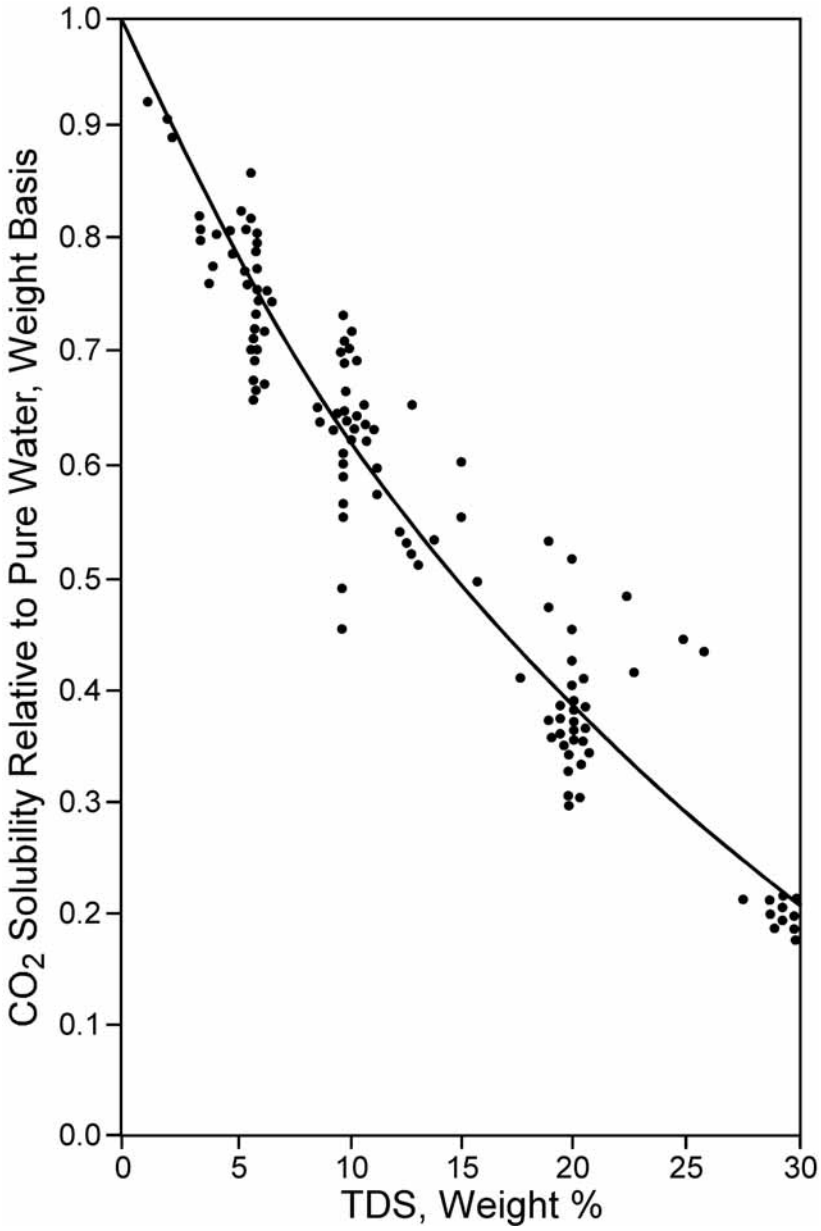

Figure AI.7. Solubility of CO_2 in brine relative to that in pure water, showing experimental points reported by Enick and Klara, 1990, and correlation developed by those authors. (TDS stands for total dissolved solids).

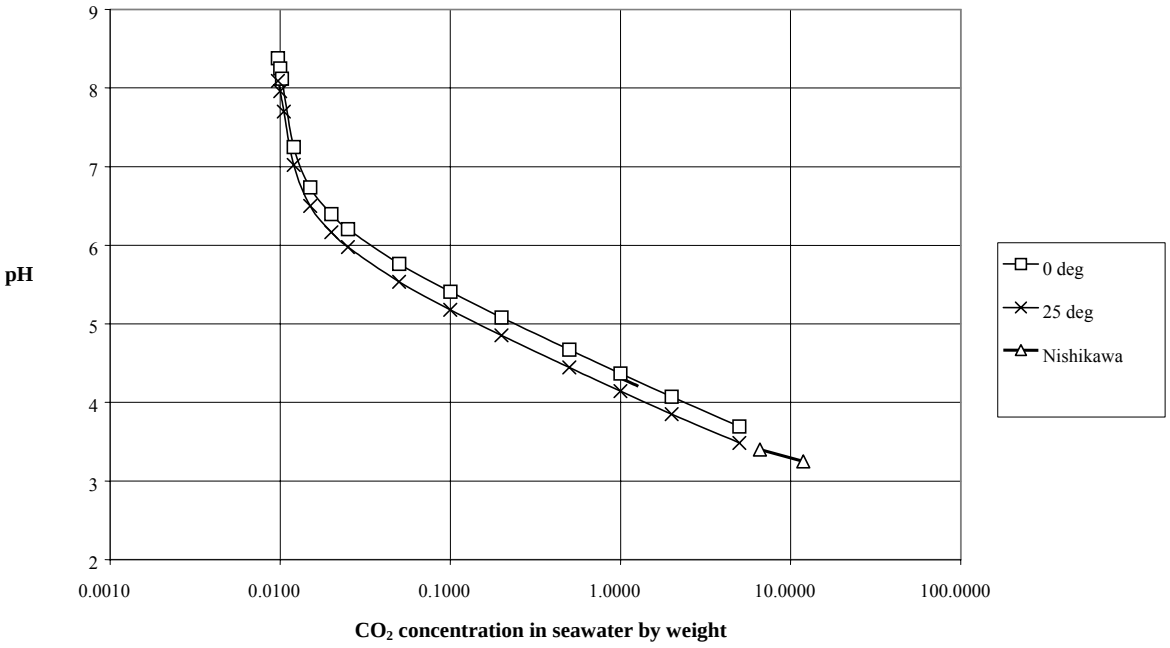

Figure AI.8. Dependence of pH on CO_2 concentration in seawater.

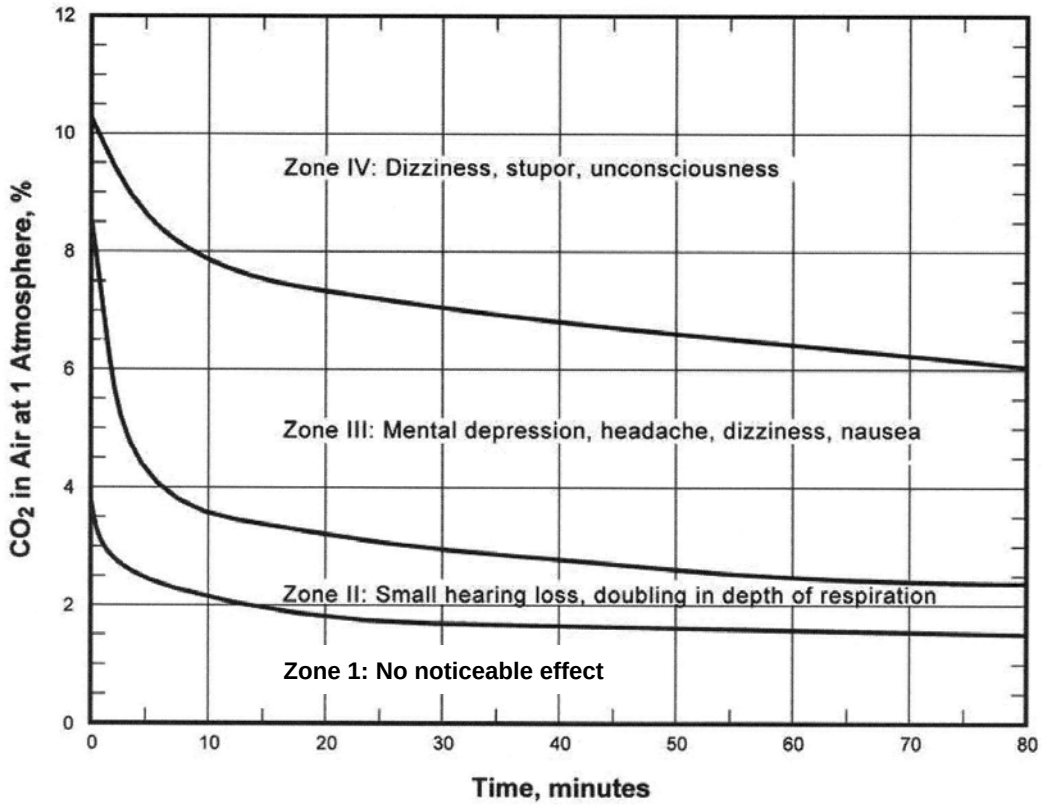

Figure AI.9. Effects of CO_2 exposure on humans (Fleming *et al.*, 1992).

AII Glossary, acronyms and abbreviations

Coordinating Lead Author
PHILIP LLOYD (SOUTH AFRICA)

Lead Authors
Jason Anderson (United States), Stefan Bachu (Canada), Sally Benson (United States), Peter Brewer (United States), Ken Caldeira (United States), Peter Cook (Australia), Richard Doctor (United States), Paul Freund (United Kingdom), Gabriela von Goerne (Germany), Chris Hendriks (Netherlands), Yasumasa Fujii (Japan), John Gale (United Kingdom), Balgis Osman Elasha (Sudan), Jose Moreira (Brazil), Juan Carlos Sanchez (Venezuela), Mohammad Soltanieh (Iran), Tore Torp (Norway), Ton Wildenborg (Netherlands)

No	Word/term	Description
1	Abatement	Reduction in the degree or intensity of emissions or other pollutants
2	Absorption	Chemical or physical take-up of molecules into the bulk of a solid or liquid, forming either a solution or compound.
3	Acid gas	Any gas mixture that turns to an acid when dissolved in water (Normally refers to H_2S + CO_2 from sour gas q.v.)
4	Adiabatic	A process in which no heat is gained or lost by the system
5	Adsorption	The take-up of molecules on the surface of a solid or a liquid.
6	Afforestation	Planting of new forests on lands that historically have not contained forests
7	Aluminum silicate mineral	Natural mineral such as feldspar, clays, micas, amphiboles composed of Al_2O_3 and SiO_2 plus other cations
8	Amine	Organic chemical compound containing one or more nitrogens in -NH_2, >NH or ≡N groups.
9	Anaerobic condition	Reducing condition that only supports life which does not require free oxygen
10	Anhydrite	Calcium Sulfate - The common hydrous form is called gypsum
11	Antarctic Treaty	Applies to the area south of 60 degrees South, and declares that Antarctica shall be used for peaceful purposes only
12	Anthracite	Coal distinguished by having the highest carbon content and therefore the highest rank (q.v.)
13	Anthropogenic source	Source which is manmade as opposed to natural
14	Anticline	Folded geological strata that is convex upwards
15	API	American Petroleum Institute; degree API is a measure of oil density given by (141.5/specific gravity) -131.5
16	Aquifer	Geological structure containing water which has significant permeability to allow flow and is bound by seals
17	Assessment unit	A geological province that has high petroleum potential
18	Assigned amount	The amount by which a Party listed in Annex B of the Kyoto Protocol agrees to reduce its anthropogenic emissions
19	ATR	Auto Thermal Reforming: Process in which the heat for the reaction of CH_4 with steam is generated by partial oxidation of CH_4.
20	Autoproduce	The production of electricity for own use
21	Avoided cost	The cost of reducing CO_2 emissions by one unit while producing the same amount as a reference plant without capture.
22	Basalt	A type of basic igneous rock which is typically erupted from a volcano
23	Basel Convention	UN Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, which was adopted at Basel on 22 March 1989
24	Baseline	The datum against which change is measured.
25	Basin	A geological region with strata dipping towards a common axis or centre
26	Bathymetric	Pertaining to the depth of water
27	Benthic	Pertaining to conditions at depth in bodies of water
28	Bicarbonate ion	The anion formed by dissolving carbon dioxide in water,

No	Word/term	Description
		HCO_3^-
29	Biomass	Matter derived recently from the biosphere
30	Bituminous coal	An intermediate rank of coal falling between the extremes of peat and anthracite, and closer to anthracite
31	Blow out	Refers to catastrophic failure of a well when the petroleum fluids or water flow unrestricted to the surface
32	Bohr effect	The pH dependent change in oxygen affinity of blood
33	Bottom-up model	A model that includes technological and engineering details in the analysis.
34	Boundary	In GHG accounting, the separation between accounting units, be they national, organizational, operational, business units or sectors
35	Breakeven price	The price necessary at a given level of production to cover all costs.
36	Buoyancy	Tendency of a fluid or solid to rise through a fluid of higher density.
37	Caprock	Rock of very low permeability that acts as an upper seal to prevent fluid flow out of a reservoir
38	Capillary entry pressure	Additional pressure needed for a liquid or gas to enter a pore and overcome surface tension
39	Carbon credit	A convertible and transferable instrument that allows an organisation to benefit financially from an emission reduction
40	Carbon trading	A market-based approach that allows those with excess emissions to trade that excess for reduced emissions elsewhere.
41	Carbonate	Natural minerals composed of various anions bonded to a the $CO_3^=$ cation (e.g. calcite, dolomite, siderite, limestone)
42	Casing	A pipe which is inserted to stabilize the borehole of a well after it is drilled
43	CBM	Coal Bed Methane
44	CCS	Carbon Dioxide Capture and Storage
45	CDM	Clean Development Mechanism - a Kyoto Protocol mechanism to assist non-Annex 1 countries to contribute to the objectives of the Protocol and assists Annex I countries meet with their commitments
46	Certification	In the context of carbon trading, certifying that a project achieves a quantified reduction in emissions over a given period
47	Chemical looping combustion	A process in which combustion of a hydrocarbon fuel is split into separate oxidation and reduction reactions by using a metal oxide as an oxygen carrier between the two reactors.
48	Chlorite	A magnesium-iron aluminosilicate sheet silicate clay mineral
49	Class "x" well	A regulatory classification for wells that are used for the injection of fluids into the ground
50	Claus plant	A plant that transforms H_2S into elemental sulphur.
51	Cleats	The system of joints, cleavage planes, or planes of weakness found in coal seams along which the coal fractures

No	Word/term	Description
52	CO_2-avoided	The difference between CO_2 captured, transmitted and/or stored, and the amount of CO_2 generated by a system without capture, net of the emissions not captured by a system with CO_2 capture
53	CO_2-equivalent	A measure used to compare emissions of different greenhouse gases based on their global warming potential
54	Co-benefit	The additional benefits flowing from policies that are implemented for a specific reason
55	COE	Cost of Electricity, value as calculated by Equation 1 in Section 3.7
56	Co-firing	The simultaneous use of more than one fuel in a power plant or industrial process
57	Completion of a well	Refers to cementing and perforating of casing and stimulation to connect wellbore to reservoir
58	Congruence	The quality of agreement between two entities
59	Conservative values	Parameter values selected so that a parameter, such as CO_2 leakage, is over-estimated
60	Containment	Restriction of movement of a fluid to a designated volume (e.g. reservoir)
61	Continental shelf	The extension of the continental mass beneath the ocean
62	COREX	A process for producing iron
63	Cryogenic	Pertaining to low temperatures, usually under about -100°C.
64	D, Darcy	A non-SI unit of permeability, abbreviated D, and approximately = $1\mu m^2$
65	Dawsonite	A mineral: dihydroxide sodium aluminium carbonate
66	Deep saline aquifer	A deep underground rock formation composed of permeable materials, containing highly saline fluids
67	Deep sea	The sea below 1000m depth
68	Default emissions factor	An approximate emission factor that may be used in the absence of precise or measured values of an Emissions Factor
69	Demonstration phase	Demonstration phase means that the technology is implemented in a pilot project or on a small scale, but not yet economically feasible at a full scale.
70	Dense phase	A gas compressed to a density approaching that of the liquid.
71	Dense-fluid	A gas compressed to a density approaching that of the liquid.
72	Depleted	Of a reservoir, one from which production has significantly reduced
73	Diagenesis	Processes that cause changes in sediment after it has been deposited and buried under another layer
74	DIC	Dissolved Inorganic Carbon
75	Dip	In geology, the angle below the horizontal taken by rock strata
76	Discharge	The amount of water issuing from a spring or in a stream that passes a specific point in a given period of time.
77	Discordant sequence	In geology, sequence of rock strata that is markedly different from strata above or below
78	Dolomite	A magnesium-rich carbonate sedimentary rock. Also, a magnesium-rich carbonate mineral ($CaMgCO_3$)

No	Word/term	Description
79	Double-grip packer	A device used to seal a drill string equipped with two gripping mechanisms
80	Down hole log	Record of conditions in a borehole
81	Drill cuttings	The solid particles recovered during drilling of a well
82	Drill string	The assembly of drilling rods that leads from surface to the drilling tool
83	Drive	Fluid flow created in formations by pressure differences arising from borehole operations
84	Dry ice	Solid carbon dioxide
85	Dynamic miscibility	The attainment of mixing following prolonged injection of gas into an oilfield.
86	ECBM	Enhanced Coal Bed Methane recovery; the use of CO_2 to enhance the recovery of the methane present in unminable coal beds through the preferential adsorption of CO_2 on coal.
87	Economic potential	Economic potential is the portion of technological potential for greenhouse gas emissions reductions or energy efficiency improvements that could be achieved cost-effectively through the creation of markets, reduction of market failures, increased financial and technological transfers. The achievement of economic potential requires additional policies and measures to break down market barriers.
88	Economically feasible under specific conditions	Technological development is sufficient for full-scale implementation under specific conditions, for instance a favourable tax regime, but there is not yet general market penetration.
89	EGR	Enhanced Gas Recovery, raising the recovery from a gas reservoir by injecting CO_2
90	Emission factor	A normalized measure of GHG emissions in terms of activity, e.g., tonnes of GHG emitted per tonne of fuel consumed
91	Emissions credit	A commodity giving its holder the right to emit a certain quantity of GHGs (q.v.)
92	Emissions trading	A trading scheme that allows permits for the release of a specified number of tonnes of a pollutant to be sold and bought
93	Endothermic	Concerning a chemical reaction that absorbs heat, or requires heat to drive it
94	Enhanced gas recovery	See EGR
95	Enhanced oil recovery	The recovery of oil additional to that produced naturally by fluid injection or other means
96	Entrained flow	Flow in which a solid or liquid, in the form of fine particles, is transported in diluted form by high velocity gas
97	Entrainment gas	The gas employed in entrained flow (q.v.)
98	EOR	Enhanced oil recovery; oil recovered by secondary or tertiary recovery mechanisms (q.v.)
99	Euphotic zone	The zone of the ocean reached by sunlight
100	Evaporite	A rock formed by evaporation
101	Exothermic	Concerning a chemical reaction that releases heat, such as combustion
102	Ex-situ mineralization	A process where minerals are mined, transferred to an

No	Word/term	Description
		industrial facility, contacted with carbon dioxide and processed
103	Exsolution	The formation of different phases during the cooling of an homogeneous fluid
104	Extended reach well	Borehole that is diverted into a more-horizontal direction to extend its reach
105	Extremophile	Microbe living in environments where life was previously considered impossible
106	Far field	A region remote from a signal source
107	Fault	In geology, a surface at which strata are no longer continuous, but displaced
108	Fault reactivation	The tendency for a fault to become active, i.e. movement to occur
109	Fault slip	The extent to which a fault has slipped in past times
110	FBC	Fluidized Bed Combustion - combustion in a fluidized bed (q.v.)
111	Feldspar	A group of alumino-silicate minerals that makes up much of the Earth's crust
112	FGD	Flue gas desulphurization
113	Fischer-Tropsch	A process that transforms a gas mixture of CO and H_2 into liquid hydrocarbons and water.
114	Fixed bed	A gas-solid contactor or reactor formed by a bed of stationary solid particles that allows the passage of gas between the particles
115	Flood	The injection of a fluid into an undergound reservoir
116	Flue gas	Gases produced by combustion of a fuel, that are normally emitted to the atmosphere
117	Fluidized bed	A gas-solid contactor or reactor comprising a bed of fine solid particles suspended by passing a gas through the bed at sufficiently high velocity
118	Folding	In geology, the bending of rock strata from the plane in which they were formed
119	Formation	A body of rock of considerable extent with distinctive characteristics that allow geologists to map, describe, and name it.
120	Formation water	Water that occurs naturally within the pores of rock formations.
121	Fouling	Deposition of a solid on the surface of heat or mass transfer equipment that has the effect of reducing the heat or mass transfer
122	Fracture	Any break in rock along which no significant movement has occurred.
123	Fuel cell	Electrochemical device in which a fuel is oxidized in a controlled manner to directly produce an electric current and heat
124	Fugitive emission	Any releases of gases or vapours from anthropogenic activities such as the processing or transportation of gas or petroleum.
125	FutureGen Project	US Government initiative for a new power station with low CO_2 emissions

No	Word/term	Description
126	Gas turbine	A machine in which a fuel is burned with compressed air or oxygen and mechanical work is recovered by the expansion of the hot products
127	Gasification	Process by which a carbon-containing solid fuel is transformed into a carbon- and hydrogen-containing gaseous fuel by reaction with air or oxygen and steam
128	Geochemical trapping	The retention of injected CO_2 by geochemical reactions
129	Geological setting	The geological environment of various locations
130	Geological time	The time over which geological processes have taken place
131	Geomechanics	The science of the movement of the Earth's crust
132	Geosphere	The earth, its rocks and minerals, and its waters
133	Geothermal	Concerning heat flowing from deep in the earth.
134	GHG	Green House Gases - carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydroflurocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF_6)
135	Hazardous and non-hazardous waste	Potentially harmful and non-harmful substances that have been released or discarded into the environment.
136	Hazardous waste directive	European directive in force to regulate definitions of waste classes and handling of them
137	HAZOP	HAZard and OPerability, a process followed to assess the risks of operating potentially hazardous equipment
138	Helsinki Convention	International legal convention protecting the Baltic water against pollution
139	Henry's Law	States that the solubility of a gas in a liquid is proportional to the partial pressure of the gas in contact with the liquid
140	HHV	Higher Heating Value - the energy released from the combustion of a fuel that includes the latent heat of water
141	Host rock	In geology, the rock formation that contains a foreign material
142	Hybrid vehicle	Vehicle that combines a fossil fuel internal combustion engine and an alternative energy source, typically batteries
143	Hydrate	An ice-like compound formed between water and CO2 or CH4 or similar gases
144	Hydrodynamic trap	A geological structure in which fluids are retained by low levels of porosity in the surrounding rocks
145	Hydrogeological	Concerning water in the geological environment
146	Hydrostatic	Pertaining to the properties of a stationary body of water
147	Hypercapnia	Excessively high CO_2 levels in the blood
148	Hypoxia	Having low rates of oxygen transfer in living tissue
149	Hysteresis	The phenomenon of a lagging recovery from deformation or other disturbance
150	IEA GHG	International Energy Agency - Greenhouse Gas R&D Programme
151	IGCC	Integrated Gasification Combined Cycle - power generation in which hydrocarbons or coal are gasified (q.v.) and the gas is used as fuel to drive both a gas and a steam turbine
152	Igneous	Rock formed when molten rock (magma) that has cooled and solidified (crystallized)

No	Word/term	Description
153	Immature basin	A basin in which the processes leading to oil or gas formation have started but are incomplete
154	Infrared spectroscopy	Chemical analysis using infrared spectroscope method
155	Injection	The process of forcing fluids down wells by means of pressure
156	Injection well	A well in which fluids are injected rather than produced
157	Injectivity	A measure of the rate at which a quantity of fluid that can be injected into a well
158	*In-situ* mineralization	A process where minerals are not mined, carbon dioxide is injected in the silicate formation, where it reacts with the minerals forming carbonates and silica
159	International Seabed Authority	An organization established under the 1982 UN Convention on the Law of the Sea, headquartered in Kingston, Jamaica
160	Ion	An atom or molecule that has acquired a charge by either gaining or losing electrons
161	IPCC	Intergovernmental Panel on Climate Change
162	JI	Joint Implementation - under Kyoto Protocol, allows a Party with a GHG emission target to receive credits from other Annex 1 Parties
163	Kyoto Protocol	Protocol to the United Nations Framework Convention on Climate Change, which was adopted at Kyoto on 11 December 1997
164	Leach	To dissolve a substance from a solid
165	Leakage	In respect of carbon trading, the change of anthropogenic emissions by sources or removals by sinks which occurs outside the project boundary
166	Leakage	In respect of carbon storage, the escape of injected fluid from storage
167	Levelized cost	The future values of an input or product that would make the NPV (q.v.) of a project equal to zero
168	LHV	Lower Heating Value - energy released from the combustion of a fuel that excludes the latent heat of water
169	Lignite/sub-bituminous coal	Relatively young coal of low rank with a relatively high hydrogen and oxygen content
170	Limestone	A sedimentary rock made mostly of the mineral calcite (calcium carbonate), usually formed from shells of dead organisms
171	LNG	Liquefied Natural Gas
172	Lithology	Science of the nature and composition of rocks
173	Lithosphere	The outer layer of the Earth made of solid rock, which includes the crust and uppermost mantle, up to 100km thick.
174	Log	Records taken during or after the drilling of a well
175	London Convention	On the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, which was adopted at London, Mexico City, Moscow and Washington on 29 December 1972
176	London Protocol	Protocol to the Convention which was adopted at London on 2 November 1996 but had not entered into force at the time of writing
177	Low-carbon energy carrier	Fuel that provides low fuel-cycle-wide emissions of CO_2, such as methanol

No	Word/term	Description
178	Macro-invertebrate	Small creature living in the seabed and subsoil, like earthworms, snails and beetles
179	Madrid Protocol	A protocol to the 11th Antarctic Treaty to provide for Antarctica's environmental protection
180	Mafic	Term used for silicate minerals, magmas, and rocks, which are relatively high in the heavier elements.
181	Magmatic activity	The flow of magma (lava)
182	Marginal cost	Additional cost that arises from the expansion of activity, ex. emission reduction by one additional unit
183	Maturation	The geological process of changing with time e.g. the alteration of peat into lignite, then sub-bituminous and bituminous coal then anthracite
184	Mature sedimentary basins	Geological provinces formed by deposition of particulate matter under water, which deposits have matured into hydrocarbon reserves
185	MEA	Mono-ethanolamine
186	Medium-gravity oil	Oil characterized by having a density between about 850 and 925kg/m^3 (between 20 and 30API)
187	Membrane	A sheet or block of material that selectively separates the components of a fluid mixture
188	Metamorphic	Of rocks that have been altered by heat or pressure
189	Mica	Class of silicate minerals with internal plate structure
190	Microseismicity	Seismic tremors in small scale
191	Migration	The movement of fluids in reservoir rocks.
192	Mineral trap	A geological structure in which fluids are retained by reaction of the fluid to form a stable mineral
193	Miscible displacement	Injection process that introduces miscible gases into the reservoir, so maintaining reservoir pressure and improving oil displacement
194	Mitigation	The process of reducing the impacts of any failure
195	Monitoring	The process of measuring the quantity of carbon dioxide stored and its location
196	Monte Carlo	A modelling technique in which the statistical properties of outcomes are tested by random inputs
197	Mudstone	A very fine-grained sedimentary rock formed from mud
198	MWh	Megawatt hour
199	National Greenhouse Gas Inventory	An inventory of anthropogenic emissions by sources and removals by sinks of greenhouse gases prepared by Parties to the UNFCCC
200	Natural analogue	A natural occurrence that mirrors in most essential elements an intended or actual human activity
201	Natural underground trap	A geological structure in which fluids are retained by natural processes
202	Navier-Stokes equations	The general equations describing the flow of fluids
203	Near-field	The region close to a signal source
204	NGCC	Natural Gas Combined Cycle - natural gas fired power plant with gas and steam turbines

No	Word/term	Description
205	Non-hazardous waste	Non-harmful substances that have been released or discarded into the environment.
206	NPV	Net Present Value - the value of future cash flows discounted to the present at a defined rate of interest
207	Numerical approximation	Representation of physico-mathematical laws through linear approximations
208	Observation well	A well installed to permit observation of subsurface conditions
209	OECD	Organization for Economic Co-operation and Development
210	OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic, which was adopted at Paris on 22 September 1992
211	Outcrop	The point at which a particular stratum reaches the earth's surface
212	Overburden	Rocks and sediments above any particular stratum
213	Overpressure	Pressure created in a reservoir that exceeds the pressure inherent at the reservoir's depth.
214	Oxidation	The loss of one or more electrons by an atom, molecule, or ion
215	Oxy-fuel combustion	Combustion of a fuel with pure oxygen or a mixture of oxygen, water and carbon dioxide
216	Packer	A device for sealing off a section of a borehole or part of a borehole
217	Partial oxidation	The oxidation of a carbon-containing fuel under conditions that produce a large fraction of CO and hydrogen
218	Partial pressure	The pressure that would be exerted by a particular gas in a mixture of gases if the other gases were not present.
219	pCO_2	The partial pressure (q.v.) of CO_2
220	PC	Pulverized Coal - usually of boilers fed with finely ground coal
221	Pejus level	The level in the ocean below which the functioning of animals deteriorates significantly
222	Pelagic	Relating to or occurring or living in or frequenting the open ocean
223	Perfluorocarbon	A greenhouse gas emitted during industrial or commercial operations
224	Permeability	Ability to flow or transmit fluids through a porous solid such as rock
225	Permian	A geological age dating between 290-248Myears ago
226	Phytotoxic	Poisonous to plants
227	Piezo-electric transducer	Crystals or films that are able to convert mechanical energy in electrical energy or vice versa
228	Pig	A device that is driven down pipelines to inspect and/or clean them
229	Polygeneration	Production of more than one form of energy, for example synthetic liquid fuels plus electricity
230	Pore space	Space in between rock or sediment grains that can contain fluids
231	Poroelastic	Elastic behaviour of porous media
232	Porosity	Measure for the amount of pore space in a rock
233	Post-combustion capture	The capture of carbon dioxide after combustion

No	Word/term	Description
234	POX	Partial Oxidation (q.v.)
235	Pre-combustion capture	The capture of carbon dioxide following the processing of the fuel before combustion
236	Primary legal source	Legal source not depending on authority given by others
237	Probability density function	Function that describes the probability for a series of parameter values
238	Prospectivity	Prospectivity is a qualitative assessment of the likelihood that a suitable storage location is present in a given area based on the available information; being only a perception it will change over time and with new information
239	Proven reserve	For oil declared by operator to be economical; for gas decided to be developed and produced; see Resource
240	Province	An area having separate but similar geological formations
241	PSA	Pressure Swing Adsorption - a method of separating gases using physical adsorption of one gas at high pressure and releasing it at low pressure
242	Rank	Quality criterion for coal
243	Reduction	The gain of one or more electrons by an atom, molecule, or ion
244	Reduction commitment	A commitment by a Party to the Kyoto Protocol to meet its quantified emission limit
245	Reforestation	Planting of forests on lands that have previously contained forests but that have been converted to some other use.
246	Regional scale	A geological feature that crosses an entire basin
247	Remediation	The process of correcting any source of failure
248	Renewables	Energy sources that are inherently renewable, e.g.solar energy, hydropower, wind, and biomass.
249	Rep. Value	Representative value
250	Reproductive dysfunction	Inability to reproduce
251	Reserve	A resource (q.v.) from which it is generally economic to produce valuable minerals or hydrocarbons
252	Reservoir	A subsurface body of rock having sufficient porosity and permeability to store and transmit fluids
253	Residual saturation	The fraction of the injected CO_2 that is trapped in pores by capillary forces
254	Resource	A body of a potentially valuable mineral or hydrocarbon
255	Retrofit	A modification of the existing equipment to upgrade and incorporate changes after installation
256	Risk assessment	Part of a risk-management system
257	Root anoxia	Lack, or deficiency, of oxygen in root zone
258	Root zone	Part of the soil in which plants have their roots
259	Safe Drinking Water Act	An Act of US Congress originally passed in 1974 that regulates *inter alia* possible contamination of underground water
260	Saline formation	Sediment or rock body containing brackish water or brine
261	Saline groundwater	Groundwater, in which salts are dissolved
262	Sandstone	Sand that turned into a rock due to geological processes
263	Saturated zone	Part of the subsurface that is totally saturated with groundwater

No	Word/term	Description
264	Scenario	A plausible description of the future, based on an internally consistent set of assumptions about key relationships and driving forces
265	SCR	Selective catalytic reduction
266	Scrubber	A gas-liquid contacting device for purification of gases or capture of a gaseous component
267	Seabed	Borderline between the free water and top of the bottom sediment
268	Seal	An impermeable rock that forms a barrier above and around a reservoir such that fluids are held in the reservoir.
269	Secondary recovery	Recovery of oil by artificial means after natural production mechanisms like overpressure have ceased.
270	Sedimentary basin	Natural large-scale depression in the earth's surface that is filled with sediments
271	Seismic profile	A two-dimensional seismic image of the subsurface
272	Seismic technique	Measurement of the properties of rocks by the speed of sound waves generated artificially or naturally
273	Seismicity	The episodic occurrence of natural or man-induced earthquakes
274	Selexol	A commercial physical absorption process to remove CO_2 using glycol dimethylethers
275	Shale	Clay that has changed into a rock due to geological processes
276	Shift convertor	A reactor in which the water- gas shift reaction, $CO + H_2O = CO_2 + H_2$, takes place
277	Simplex orifice fitting	An apparatus for measuring the flow rate of gases or liquids
278	Sink	The natural up-take of CO_2 from the atmosphere, typically in soils, forests or the oceans.
279	SMR	Steam Methane Reforming - a catalytic process in which methane reacts with steam to produce a mixture of H_2, CO and CO_2
280	SNG	Synthetic natural gas. Fuel gas with a high concentration of methane produced from coal or heavy hydrocarbons
281	SOFC	Solid Oxide Fuel Cell - a fuel cell (q.v.) in which the electrolyte is a solid ceramic composed of calcium- or yttria–stabilized zirconium oxides
282	Soil gas	Space in soil grains that contain gas (air)
283	Soil gas	Gas contained in the space between soil grains
284	Solubility trapping	A process in which fluids are retained by dissolution in liquids naturally present
285	Sour gas	Natural gas containing significant quantities of acid gases like H_2S and CO_2
286	Source	Any process, activity or mechanism that releases a greenhouse gas, an aerosol, or a precursor thereof into the atmosphere
287	Speciation	The determination of the number of species into which a single species will divide over time
288	Spill point	The structurally lowest point in a structural trap (q.v.) that can retain fluids lighter than background fluids.
289	Spoil pile	Heap of waste material derived from mining or processing operations

No	Word/term	Description
290	SRES	Special Report on Emissions Scenarios - used as a basis for the climate projections in the TAR (q.v.)
291	Stabilization	Relating to the stabilization atmospheric concentrations of greenhouse gases.
292	Steam reforming	A catalytic process in which a hydrocarbon is reacted with steam to produce a mixture of H_2, CO and CO_2
293	Storage	A process for retaining captured CO_2 so that it does not reach the atmosphere
294	Strain gauge	Gauge to determine the deformation of an object subjected to stress
295	Stratigraphic	The order and relative position of strata
296	Stratigraphic column	A column showing the sequence of different strata
297	Stratigraphic trap	A sealed geologic container capable of retaining fluids, formed by changes in rock type, structure or facies.
298	Stimulation	The enhancement of the ability to inject fluids into, or recover fluids from, a well
299	Stripper	A gas-liquid contacting device, in which a component is transferred from liquid phase to the gas phase,
300	Structural trap	Geologic structure capable of retaining hydrocarbons, sealed structurally by a fault or fold.
301	Structure	Geological feature produced by deformation of the Earth's crust, such as a fold or a fault; a feature within a rock such as a fracture; or, more generally, the spatial arrangement of rocks.
302	Structure contour map	Map showing the contours of geological structures
303	Subsoil	Term used in London and OSPAR conventions, meaning the sediments below the seabed
304	Sub-bituminous coal	Coal of a rank between lignite (q.v.) and bituminous (q.v.) coal
305	Sustainable	Of development, that which is sustainable in ecological, social and economic areas
306	Supercritical	At a temperature and pressure above the critical temperature and pressure of the substance concerned
307	Syngas	Synthesis gas q.v.
308	Synthesis gas	A gas mixture containing a suitable proportion of CO and H_2 for synthesis of organic compounds or combustion
309	Synfuel	Fuel, typically liquid fuel, produced by processing fossil fuel
310	Tail gas	Effluent gas at the end of a process
311	Tailing	The waste resulting from the extraction of value from ore
312	TAR	Third Assessment Report of the Intergovernmental Panel on Climate Change
313	TCR	Total capital requirement
314	Technical Potential	The amount by which it is possible to reduce greenhouse gas emissions by implementing a technology or practice that reached the demonstration phase.
315	Tectonically active area	Area of the Earth where deformation is presently causing structural changes
316	Tertiary	Geological age, dating from about 65 to 2 million years ago

No	Word/term	Description
317	Tertiary recovery	Oil generated by a third method; the first is by pressure release or depletion, and the second by oil driven out by injection of water
318	Thermocline	The ocean phenomenon characterized by a sharp change in temperature with depth
319	Thermohaline	The vertical overturning of water masses due to seasonal heating, evaporation, and cooling
320	Top-down model	A model based on applying macro-economic theory and econometric techniques to historical data on consumption, prices, etc
321	Toxemia	Poisoning, usually of the blood
322	Toxicology	Scientific study of poisons and their effects
323	Tracer	A chemical compound or isotope added in small quantities to trace flow patterns
324	Transaction cost	The full cost of transferring property or rights between parties
325	Trap	A geological structure that physically retains fluids that are lighter than the background fluids like an inverted cup
326	Ultramafic rocks	An igneous rock consisting almost entirely of iron- and magnesium-rich minerals with a silica content typically less than 45%
327	UNCLOS	United Nations Convention on the Law of the Sea, which was adopted at Montego Bay on 10 December 1982
328	Unconformity	A geological surface separating older from younger rocks and representing a gap in the geologic record.
329	Under-saturated	A solution that could contain more solute than is presently dissolved in it.
330	UNFCCC	United Nations Framework Convention on Climate Change, which was adopted at New York on 9 May 1992
331	Updip	Inclining upwards following a structural contour of strata
332	Upper ocean	The ocean above 1000m depth
333	Vacuum residue	The heavy hydrocarbon mixture that is produced at the bottom of vacuum distillation columns in oil refineries
334	Vadose zone	Region from the water table to the ground surface, also called the unsaturated zone because it is partially water saturated
335	Validation	In the context of CDM (q.v.), the process of independent evaluation of a project by a designated operational entity against set requirements
336	Ventilation	The exchange of gases dissolved in sea water with the atmosphere, or gas exchange between an animal and the environment
337	Verification	The proving, to a standard still to be decided, of the results of monitoring (q.v.): In the context of CDM, the independent review by a designated operational entity of monitored reductions in anthropogenic emissions
338	Viscous fingering	Flow phenomenon arising from the flow of two largely immiscible fluids through a porous medium.
339	Well	Manmade hole drilled into the earth to produce liquids or gases, or to allow injection of fluids
340	Well with multiple	Well drilled with multiple branching holes and more than one

No	Word/term	Description
	completions	hole being made ready for use
341	Well-bore annulus	The annulus between the rock and the well casing
342	Wellhead pressure	Pressure developed on surface at the top of the well
343	Wettability	Surface with properties allowing water to contact the surface intimately
344	Zero-carbon energy carrier	Carbon-free energy carrier, typically electricity or hydrogen.