A CHEMICAL SENSOR TO AID IN THE SEARCH FOR UNDERWATER ARCHAEOLOGICAL SITES

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ABSTRACT

This paper investigates the potential application of underwater chemical sensors to underwater archaeology. A model is explained that demonstrates that in ideal circumstances certain archaeologically important metals, namely iron, copper, tin, lead, and silver, corroding in seawater may be detectable using current technology. A design for a copper and iron in situ underwater chemical sensor, which uses chemiluminescence detection methods, and its integration into the AUV REMUS is proposed. A description of the next steps of this project and an overview of other uses for this sensor is included.

1. INTRODUCTION

It is a very challenging task to locate underwater archaeological sites. Underwater archaeologists have to work with both oceanographers and engineers to develop efficient and cost effective means of surveying the ocean to look for shipwrecks and other evidence of the human past. Sonar surveys often produce hundreds of potential archaeological sites—some of which are meaningful and most of which are simply anomalies on the sea floor, trash, or nothing at all. Scientists must dig through data and, oftentimes, arbitrarily choose which sites are worth a second look.

Using another sensor in conjunction with a sonar system in an underwater archaeological survey could provide scientists with more information about each individual site and allow them to make better decisions about which sites to go back to. An underwater chemical sensor, which is able to detect certain metals in seawater, used in conjunction with a side-scan sonar system, should be able to detect the chemical signatures of the materials on board a sunken ship and/or the materials the ship is made from. While sonar data only gives us an idea of the seafloor relief, chemical data should give us an idea of what materials are on a site. Importantly, a chemical survey does not require that we disturb the sediments or archaeological artifacts. Collecting chemical data and sonar data simultaneously should be a more efficient way to look for underwater archaeological sites. Moreover, it should also be more cost effective because chemical data has the potential to eliminate many of the later, more thorough investigations of target sites which end up in the discovery of mounds of rocks.

This paper proves the concept that it would be useful and feasible to build a chemical sensor to aid in underwater archaeological searches. It includes a summary of the archaeological and chemical investigation that has been conducted in order to choose which materials would be best to attempt to chemically sense in seawater. It also presents a simplified model that determines whether or not the chosen materials might be observable in the vicinity of a shipwreck. Then, it explains which environments would be most appropriate for conducting such a search. Based on this data and current technology in the field of underwater chemical sensing it proposes the design of an underwater copper and iron sensor that uses chemiluminescence detection methods and is able to take chemical measurements in situ continuously, autonomously, and unobtrusively. It includes a method for integrating this sensor into the REMUS, a small Autonomous Underwater Vehicle (AUV). Finally, it lays out the next steps of this project and several of the other potential applications of this sensor.

2. A CHOICE OF MATERIALS TO DETECT

In choosing which materials to detect it is important to remember that the chosen materials must not only be historically prevalent on shipwrecks but they must also have chemical principles that allow for their corrosion and adequate dispersion in seawater. In general, ships have been made of and carried both organic materials and metals. However, this paper only analyzes metals because they last much longer than organic materials in oxygenated water.

2.1 Archaeological Reasons

In antiquity only a handful of metals were intentionally used and understood. These include iron, tin, copper, lead, silver, and gold (Hamilton 1998). During the Bronze Age, the materials for bronze, copper and tin, were traded across the Mediterranean as oxhide-shaped ingots. Two Bronze Age shipwrecks feature these archaeological artifacts. At Cape Gelidonya 34 copper ingots were found weighing an average of 25 kg a piece (Pedersen 2002a). At the Uluburun shipwreck, archaeologists found 11 tons of metal—10 tons were copper and 1 ton was tin (Pedersen 2002b). Moreover, Cemal Pulak tells us, "Copper ingots have been found all over the Mediterranean Shoreline, reflecting two facts: first, that most large-scale trade was shipbourne; and second that copper ingots were an acceptable form of currency" (Pulak 1999).

In antiquity, silver and gold were transported across the Mediterranean in its raw form, as coins, and as jewelry. Moreover, raw silver and gold were transported in large quantities from the Americas to Europe in more recent times. During Roman times, lead was used for anchors and ship ballast, and also in making pewter, which was commonly traded across the Mediterranean. Lead weights, cannonballs, sheeting, and stripping are commonly found on underwater archaeological sites. Iron is the most common metal found on archaeological sites (Hamilton 1998). It was used to make weapons and tools, and also fasteners and braces for ships.

Therefore, archaeology tells us that the materials we should attempt to look for are iron, tin, copper, lead, silver, and gold.

2.2 Chemical Reasons

It is important to reach a balance between a corrosive material (so that it emits enough particles into the water column for a sensor to detect) and a material that is somewhat resistant to corrosion (so that the material will not have completely corroded away by the time the site is analyzed). Gold does not corrode in seawater. However, iron, tin, copper, lead, and silver all do. In general, their corrosion potential from least to most corrosive is: silver, copper, lead, tin, and iron (Hamilton 1998). However, the actual rate at which these metals corrode is greatly affected by a variety of environmental factors making it incredibly difficult to predict the amount of corrosion products in the water column around an underwater archaeological site. These factors include oxygen levels, sedimentation and seafloor composition, temperature, pH, depth, current velocity, and plant/animal life. Also, placing two different metals together can affect their corrosion rates. In general, adding a less noble metal to a more noble metal decreases the corrosion rate of the more noble metal (Brown 2002). This is why zinc is often used in conjunction with steel as a sacrificial anode.

Corrosion rates are generally not constant over time. Usually corrosion rates decrease exponentially. This is sometimes because of the fact that corrosion by-products can protect the material. For instance, a film of cuprous oxide often forms on corroding copper and protects it from further corrosion (Boyd and Fink 1978). Also, it is possible that metals could go into static equilibrium with their environment. Furthermore, corrosion is not consistent. Slightly different alloys, thicknesses, mechanical stress, impurities, and differences in manufacturing techniques can all drastically affect corrosion rates. In one case, during an excavation in Tel Abu Hawam, Israel, a pair of bronze cymbals was found on the ocean floor. While one was almost corroded away the other was in very good condition (Fox 1994). All and all, this means that there is a wide range of expected corrosion rates for every metal and any approximations made about corrosion should take this fact into consideration.

3. A CORROSION MODEL

The purpose of this model is to demonstrate that it is reasonably likely to detect corroding materials on shipwrecks. Therefore, this model assumes somewhat ideal conditions for corrosion and dispersion into seawater. It is also useful in determining which materials more worth pursuing than others.

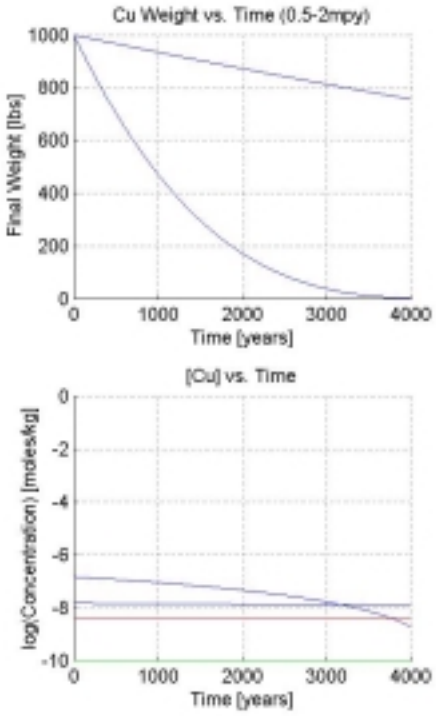
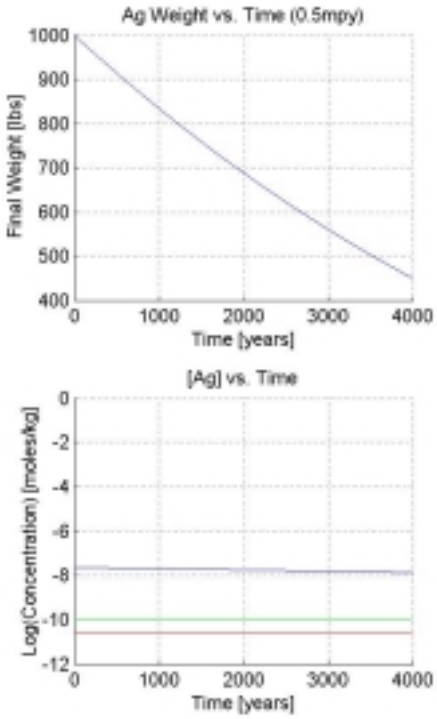


Figure 1a.



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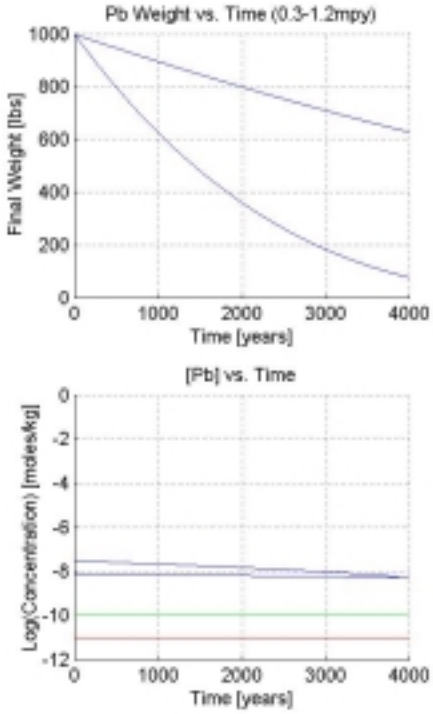

Figure 1b.

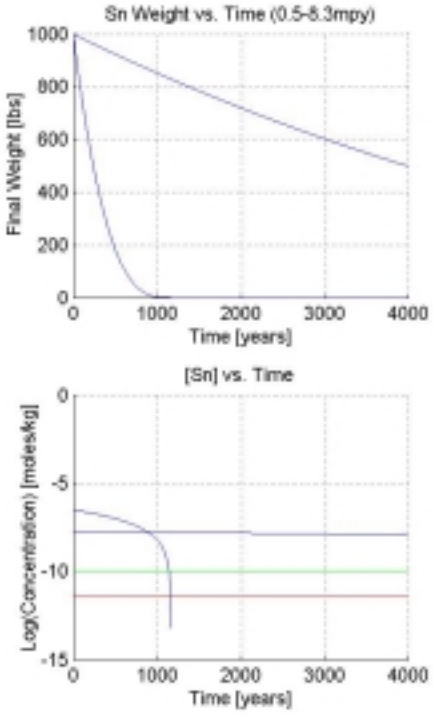

Figure 1d.

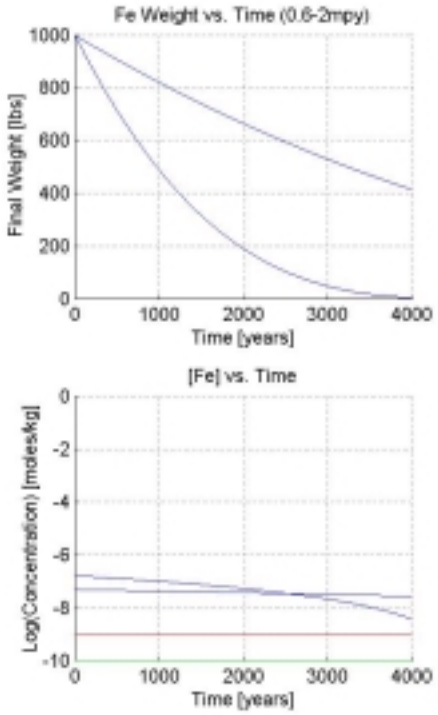

Figure 1e.

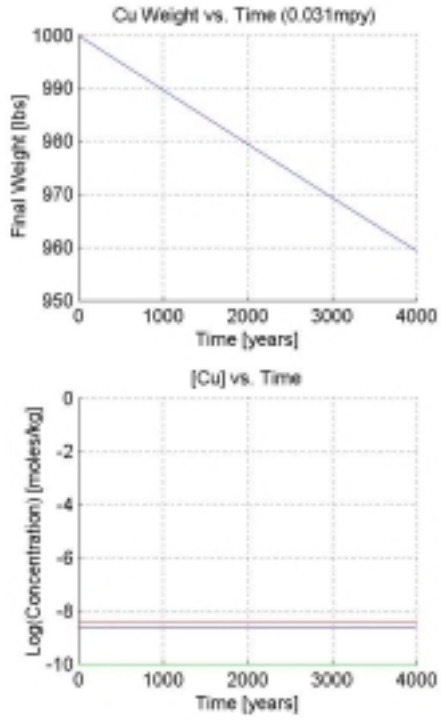

Figure 1f.

Figure 1 (a-f). In each case, in the top graphs, the blue line depicts the weight of the metal over time caused by corrosion. In the bottom graphs the blue line depicts the log of the concentration of the metal in seawater over time caused by corrosion. The red line indicates the average background concentration of the metal in seawater (Pilson 1998). The green line indicates the assumed detection threshold of 0.1 nmol/kg. The corrosion rates (in mils per year where 1 mil is 0.001 of an inch) used in graphs a-e are indicated in the heading of each graph and are taken from Corrosion of Metals in Marine Environments (Boyd and Fink 1978). The corrosion rate used in graph f is indicated in the heading of that graph and is based on conjectures made by Cemal Pulak (Pulak 1999). The scales are not the same between the graphs. Also, important to note is that the value given for silver is not firmly established and it likely that that value should be much lower.

3.1 Assumptions and Method

The model used is a simple box model, which assumes a 1000 lb spherical source. Also, it assumes that as particles are corroded away from the source they enter a one meter cubed box. The particles are equally distributed within this box such as in a well-mixed benthic boundary layer (Hanson and Donaghay 1998). The flux of seawater through the box, which is the driving force for the movement of particles in this model, is 0.001 meters cubed per second, which indicates that the water surrounding the archaeological site is relatively stagnant such as in a basin. It is assumed that the material corrodes uniformly at the given corrosion rates and that the rate stays the same over time.

Figure 1 (a-f) includes the data that was derived from running this model with each of these five metals. Each includes a graph of the material's weight over time and a graph of the concentration of the material within the one meter cubed box. The corrosion rates used are indicated at the top of the graphs. In Figure 1 (a-e), the rates are taken from Boyd and Fink (1978) and generally based upon averages from a sixteen-year study. The corrosion rate for silver is not well substantiated and should probably be lower. In Figure 1(f), the corrosion rate is taken from a conjecture made by Cemal Pulak (1999) based on analysis of copper ingots from the Uluburun Shipwreck. In each case the average seawater background concentration of the metal is plotted in red and assumed constant over time (Pilson 1998). Moreover, an approximate detection threshold of 0.1nmol/kg is plotted in green. Importantly, the concentrations of trace metals due benthic flux are many orders of magnitude less than the concentrations of trace metals caused by the corrosion of archaeological artifacts as taken from this model (Riley and Chester 1976).

It is important to remember that there are many other things that affect trace metal concentrations in seawater including dispersion, speciation, and complexation. In this model both the hydrodynamics of particle dispersion and chemical interactions have been neglected in order to drastically simplify the

calculations and produce a picture of the best-case scenario. A more precise model of this situation could be created in the future in order to analyze many more of the factors that affect the concentrations of trace metals in seawater. For instance, Applied Science Associates works on the reverse problem of determining where a chemical may be coming from in the marine environment based on the specific hydrodynamics of that area.

3.2 Results of the Model

3.2.1 Analyzing the Graphs

As seen in Figures 1 (a-e) the concentration of each metal caused by corrosion is much higher than both the background concentration and the detection threshold, at least initially. In all cases, because of the decreasing size of the object over time, the concentrations taper out. Therefore, detectable concentrations of these metals in seawater might exist for more than 4,000 years. Of course, because of the assumptions in the model, this is an upper bound.

In Figure 1 (f) the concentration of copper caused by corrosion is less than the background concentration. This is because the corrosion rate derived from assumptions made by Cemal Pulak (1999) is much lower than published corrosion rates given by Boyd and Fink (1978). It is likely that the corrosion rates experienced by these ingots probably diminished drastically over the 3300 years. This means that the copper concentration in the seawater at present would be much lower than the model has predicted.

Another possibility is that the environment that the ingots were found in is not conducive to corrosion and therefore these ingots have actually corroded at this very low rate for the entire time they have been submerged. Unfortunately, no chemical study as been performed on the site to determine if the ingots are still leaching corrosion products into the seawater. However, if this model does in fact illustrate the corrosion rate and subsequent concentrations of copper in the seawater surrounding the Uluburun shipwreck and if a sensor was accurate to 0.1nmol/kg it could potentially sense these copper ingots. Not only are there more than 1,000 pounds of copper on the seafloor in this location, but also the sensor would detect the concentration of copper caused by corrosion added to the background concentration, which, in turn would be perceptibly higher than the background concentration alone.

Therefore, this model demonstrates that it may be possible to detect all of these corroding materials in seawater under ideal environmental conditions if there was enough of the material present on the seafloor.

3.2.2 The Best Environment

This model demonstrates that the ideal environment for the operation of an underwater chemical sensor for archaeological purposes is one that allows for average corrosion rates, meaning that oxygen level, depth, pH, sediment composition, and temperature are all moderate. Low background concentrations of the trace metals are desirable. Moreover, the best environment would also have relatively stagnant water and exhibit a strong well-mixed benthic boundary layer. Anoxic waters are not ideal because metals corrode very quickly in such environments.

4. SENSOR DESIGN

4.1 A Final Choice of Materials to Detect

Despite the fact that there is good reason to design a sensor to detect iron, copper, lead, tin, and silver, it is necessary to narrow down this list to metals that are detectable using current technology. An easy method of detection must be available for each metal chosen, and that method must be adaptable for in situ operation. Moreover, the method must have a low enough detection threshold for this application. Currently few methods exist which can accurately and easily detect silver and tin concentrations in seawater. Moreover, though methods for the detection of lead in water do exist they are mostly for freshwater and not exceptionally sensitive. Methods do exist for copper and iron, as these metals are important to detect in seawater because of iron's biological importance and copper's environmental importance. Table 1 summarizes each of the factors taken into account in order to narrow down the list of metals to detect. Based on all of these factors a design for a copper and iron sensor is proposed.

Table 1. A Comparison of Several Different Archaeologically Important Metals

	Corrosion Potential (Concentration of Metal)	Residency on Seafloor	Archaeological Likelihood of Discovery (in Large Quantities)	Reliable Seawater Detection Method That Could be Used for In Situ Measurements
Gold	None	Long	Low	No
Silver	Low	Long	Low	No
Copper	Medium	Medium	Medium	Yes
Lead	Medium	Medium	High	No
Tin	High	Short	Low	No
Iron	High	Short	High	Yes

4.2 Method of Detection

Several possible detection methods have been explored in designing an in situ underwater copper and iron sensor. Importantly, in order for this sensor to be appropriate to this application it needs to be simple and precise. It must have very good time resolution and therefore must not preconcentrate the sample or analyze it in batches. Rather a continuous flow-through method is ideal. The many methods for detection of trace metals in seawater include chemiluminescence, fluorescence, spectophotometry, and electrochemical methods (Buffle and Horvai 2000). In order to ensure appropriate time resolution electrochemical methods have been ruled out. Moreover, without preconcentration both spectophotometry and fluorescence do not produce the precision needed for this application. Fortunately, chemiluminescence has both very good accuracy and resolution. The only downside to this method is that in order to analyze some metals a large number of reagents are required. Fortunately, for both copper, and iron, the number of reagents required is relatively small. The bench top chemiluminescent method for copper established by O'Sullivan et al (1995) and the bench top method for iron established by Sunda and Hunstman (1991) produce both the resolution and precision that are needed for this application and importantly are easy to implement in situ. These methods and a description of how they can be converted them from bench top methods to in situ methods is described in Section 4.4 of this paper.

4.3 Design Parameters

A copper and iron sensor used for underwater archeological searching could be designed for integration into a variety of different vehicles and instruments, such as AUVs and Remotely Operated Vehicles (ROVs), and used in conjunction with a multitude of other sensors, such as sonar systems and sub-bottom profilers. Because engineers hope to use AUVs to do archaeological sonar searches more efficiently in the future (Mindell and Bingham 2001), this chemical sensor has been designed for integration into the REMUS, Remote Environmental Monitoring UnitS, a small AUV created by the Wood's Hole Oceanographic Institution. It is equipped with a side-scan sonar system. The benefit of using this AUV is that its nose and hull can detach, so that an extra hull section containing a sensor can be inserted. This sensor can rely on the power provided by REMUS and can also transmit and accept data from the AUV. REMUS is 52 inches long and 7.5 inches in diameter.

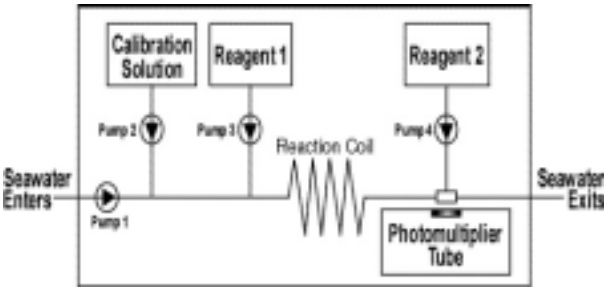

Figure 2. This block diagram depicts the general flow design of the sensor. The seawater enters the device and can be mixed with a calibration solution it calibration is deemed necessary. It then mixes with the first reagent and a reaction can take place in a reaction coil. The second reagent is added and this reaction produces light that the photomultiplier tube measures. The seawater exits.

4.4 Mechanical, Electrical, and Fluidics Design

A detailed design of a copper and iron sensor has been created along with several block diagrams showing the fluidic and electronics of the system. Based on the two chemiluminescent methods chosen a flow-through copper and iron detection scheme was developed. Figure 2 shows the flow design that will be replicated for each metal. For copper, reagent 1 is 5% H_2O_2 in addition to acid in order to lower the pH of the solution to 3 to free copper from organic ligands. Reagent 2 is CEDAB, 1,10 penanthroline, TEPA, and sodium hydroxide. The detection limit for this method is 0.06nmol/kg (O'Sullivan et al 1995). For iron, reagent 1 is an optional solution to reduce Fe (III) into Fe (II) in order to acquire a total iron amount if desired. Reagent 2 is luminol, potassium hydroxide, and boric acid. The desired pH for this reaction is 9.9 and the detection limit is 0.05nmol/kg (Sunda and Huntsman 1991). In each case a calibration solution allows the device to be calibrated in situ.

Similar to Figure 2, Figure 3 is a plumbing diagram that was created to demonstrate the actual parts needed for this system. The photomultiplier tubes (PMT) chosen are from Hamamatsu's HC120 Series. They are able to measure the intensity of light produced in a chemical reaction, and this intensity corresponds to the concentration of the metal in the seawater.

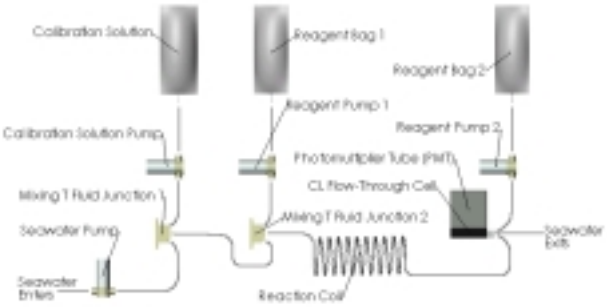

Figure 3. This plumbing diagram is similar to Figure 2 to but shows the actual parts that the sensor will be created from.

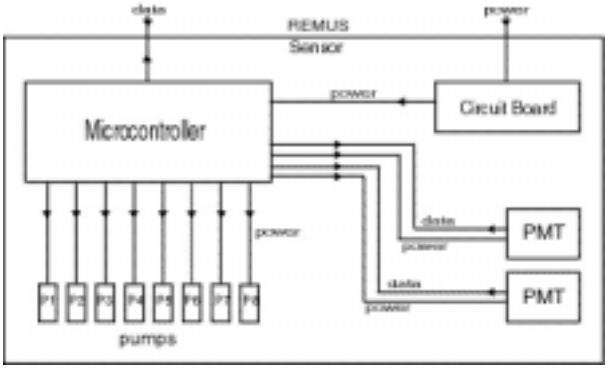

Figure 4. This block diagram depicts the general electronics design of the sensor. The power is received from the REMUS. The sensor and the REMUS can transmit data to each other. The power is regulated through the circuit board and then sent to a microcontroller. The microcontroller sends power to the pumps and photomultiplier tubes and the photomultiplier tubes, in turn, send data back to the microcontroller. Information gathered is stored on the microcontroller.

The pumps are Bio-Chem Valve Inc. Series 090SP mircopumps. The flow-through cell can be obtained through Hellma Worldwide. The junctions, coils, and tubing can be purchased from Upchurch Scientific.

Next an electronics scheme was created which shows the power and data transfer between the various parts of the sensor (Figure 4). While the sensor communicates with and gets its power from REMUS, it stores its data on a Persistor CF2 microcontroller. This microcontroller also controls the action of the pumps and PMTs. The circuit board, which will serve as a power converter, not yet been designed.

The whole system was assembled in order to fit into a six-inch REMUS hull section (Figure 5). The top half of this system, which holds the electronics and fluidics, is dry and the bottom half, which holds the reagent bags, is flooded so that the reagents will be at the same pressure as the seawater. The six-inch REMUS hull section containing this sensor is shown in Figure 6. Its door and filter allow seawater to flood half of the sensor and also allow for the collection of seawater samples to be analyzed. Figure 7 shows how the sensor fits into the REMUS and Figure 8 shows what REMUS will look like with the sensor added. A buoyancy evaluation was performed and this sensor will be positively buoyant therefore will have to be ballasted.

4.5 Design Limitations

Limitations on this device include a depth limit dependant upon the fluidics and electronics. Also, in order to detect chemical plumes caused by corroding materials on shipwrecks the sensor will have to travel fairly closely along the seafloor. Proximity to the seafloor may be limited by the side-scan sonar on the REMUS.

4.6 Other Design Options

This design is just one path that could be taken in building such a sensor. In the future micro-electrical mechanical (MEMs) devices could be used in fluidics systems in order to decrease the overall size of the sensor (Figure 9). However, it seems as though MEMs, specifically pumps and valves, are not yet sophisticated enough for this particular sensor. There are also troubles with purging bubbles from MEMs fluidics systems (Buffle and Horvai 2000).

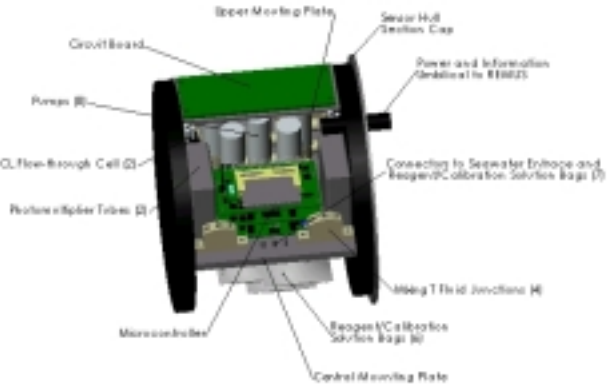

Figure 5. This diagram depicts the sensor and all of its components, both electric and fluidic, as it might fit into a six-inch REMUS hull section. The top half of this sensor contains the electronics and fluidics and is dry. The bottom half contains the reagent bags and is flooded.

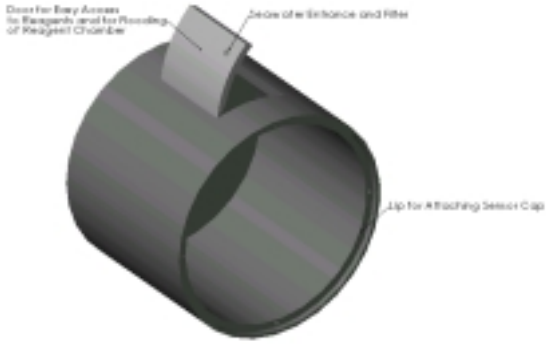

Figure 6. This diagram depicts the sensor housing, a six-inch REMUS hull section. This hull section is equipped with a door for access to the reagent bags and a filter for the intake of samples.

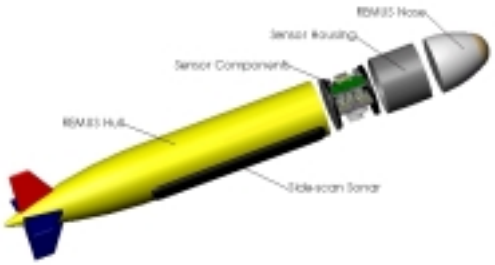

Figure 7. This diagram depicts the REMUS and the iron and copper sensor as they would fit together.

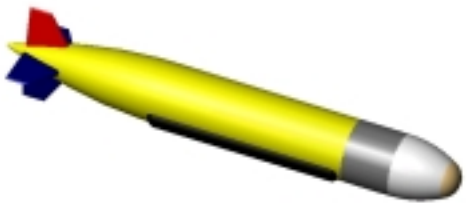

Figure 8. This diagram depicts the assembled REMUS.

5. DISCUSSION

5.1 Archaeological Benefits of this Research

The development of an iron and copper sensor for use in underwater archaeology would be an important advancement in the field and make searching for underwater archaeological sites more time efficient and cost effective. This technology would allow us to gather chemical data in addition to sonar data the sea without intrusion into the sediment. This is especially important on archaeological sites where disturbing the sediment could lead to the loss of archaeological information. Beyond searching for archaeological sites, such a device could also be used to chemically analyze previously found archaeological sites or even search around sites to look for hidden artifacts. Therefore, a copper and iron sensor has several archaeological applications.

5.2 Where to go From Here

The next steps in this project include performing a bench top experiment of the proposed sensor in order to determine if, as designed, it has the accuracy and time resolution needed. Then, it will be necessary to order the parts for the in situ sensor and build it. After this it must be integrated into REMUS and field-tested. Finally, it should be tested on known underwater archaeological sites and then used to look for new ones.

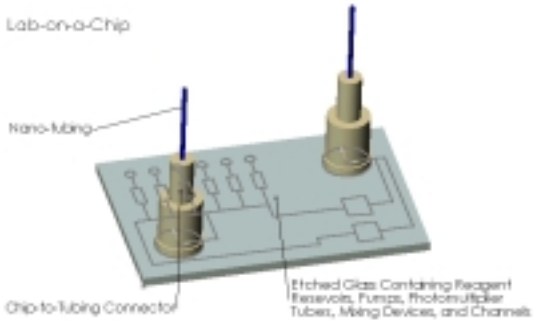

Figure 9. This diagram depicts a lab-on-a-chip, a fluidics MEMs device. In the future the sensor proposed in this paper could be created using MEMs technology and significantly smaller than the proposed design.

5.3 Other Benefits of this Research

This research also benefits other marine-related fields. For instance, an underwater chemical sensor could be used for environmental purposes. Since copper is hazardous to life, a copper sensor would be useful in detecting the sources of copper pollution in the sea. There are also industrial benefits to building a chemical sensor. For instance, it could be used to search for and inspect underwater piping, oil platforms, and other underwater structures. Lastly, it could be used for military purposes such as the detection of mines and submarines, and the inspection of underwater military structures.

6. CONCLUSIONS

In conclusion this paper has included an analysis of the usefulness of underwater chemical sensors in underwater archaeology. An underwater chemical sensor used on an AUV equipped with side-scan sonar should be able to provide scientists with important information about the potential location of archaeological sites in the sea. This should be a cost effective and efficient way to conduct an underwater archaeological survey.

REFERENCES

BOYD, W. K. and F. W. FINK. *Corrosion of Metals in Marine Environments.* Columbus, OH: Metals and Ceramics Information Center, 1978.

BROWN, RICHARD. *Corrosion and Corrosion Control: Class Notes*. University of Rhode Island, Chemical Engineering Course 534, 2002.

BUFFLE, J. and G. HORVAI. *In situ Monitoring of Aquatic Systems: Chemical Analysis and Speciation.* Chichester: John Wiley & Sons, 2000.

FOX, G. L. “Cupreous Metal Corrosion at a Bronze Age Coastal Marine Archaeological Site: A Study of Site Processes at Tel Nami, Israel.” *The International Journal of Nautical Archaeology*. V23n1 (1994): 41-47.

HAMILTON, D. L. “Methods of Conserving Underwater Archaeological Material Culture.” *Conservation Files: ANTH 605, Conservation of Cultural Resources I*. Nautical Archaeology Program, Texas A&M University, WWW: http://nautarch.tamu.edu/class/ANTH605, 1998.

HANSON, A. K. and P. L. DONAGHAY. “Mirco- to Fine- Scale Chemical Gradients and Layers in Stratified Coastal Waters.” *Oceanography*. V11n1 (1998): 10-17.

MINDELL, D.A. and B. BINGHAM, “New Archaeological Uses of Autonomous Undersea Vehicles.” *IEEE "Oceans" Engineering Conference*. 2001.

O’SULLIVAN, D. et al. “Stopped Flow Luminol Chemiluminescence Determination of Fe (II) and Reducible Iron in Seawater at Subnanomolar Levels.” *Marine Chemistry*, V49 (1995): 65-77.

PEDERSEN, R. K. “Bronze Age Shipwreck Excavation at Cape Gelidonya.” Institute of Nautical Archaeology. WWW: http://ina.tamu.edu/capegelidonya.htm, 2002a.

PILSON, M. E. Q. *An Introduction to the Chemistry of the Sea*. Upper Saddle River, NJ: Prentice Hall, 1998.

PEDERSEN, R. K. “Bronze Age Shipwreck Excavation at Uluburun.” Institute of Nautical Archaeology. WWW: http://ina.tamu.edu/ub_main.htm, 2002b.

PULAK, C. “Shipwreck! Recovering 3,000 Year Old Cargo.” *Archaeological Odyssey*. Sept/Oct 1999.

RILEY, J. P. and R. CHESTER, eds. *Chemical Oceanography: 2nd Edition, Volume 6*. London: Academic Press, 1976.

SUNDA, W. G. and S. A. HUNTSMAN. “The Use of Chemiluminescence and Ligand Competition with EDTA to Measure Copper Concentration and Speciation in Seawater.” *Marine Chemistry*, V36 (1991): 137-163.

AKNOWLEDGEMENTS

A special thanks to my research advisor Alfred K. Hanson at the University of Rhode Island and Subchem Systems Inc. Also thanks to Rob Pockalny, Dwight Coleman, Jeff Barnes, William DeLeo, Peter Egli, Richard Sweetman, Heather Saffert, and Peter Obuchowski at URI; Ian MacLeod and Vicki Richards at the Western Australia Maritime Museum; Brendan Foley, Richard Camilli, and Dave Mindell at MIT; and Donny Hamilton at Texas A&M for their helpful correspondence. This Research Experience for Undergraduates at the University of Rhode Island Graduate School of Oceanography was funded through a National Science Foundation Grant.