Rheological Behavior of Flocculated Suspensions of Artificial Marine Cohesive Sediment

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***Abstract*—The clay mineral type and the organic matter compositions have a strong influence on the mechanical properties of marine sediments. Understanding the viscous behavior of marine sediments composed of flocculated particles is important in many applications such as penetration of heavy objects in the cohesive seafloors and hydrodynamic transport of flocculated sediments among others. In this study, the effects of the clay and organic matter (OM) concentrations and the shear rate on the viscous behavior of the artificial flocs, similar to the ones that are found in the seabed, are studied. It was found that the addition of guar gum increases the viscosity of the floc suspensions significantly. The behavior appears to change from near-Newtonian at low OM concentration to mildly shear-thinning at high OM values. An empirical model was developed that allows to calculate the viscosity of the floc suspensions as a function of clay content, organic matter content and shear rate.**

Keywords—Montmorillonite; guar gum; viscosity; flocculation; rheology

I. Introduction

Decomposition of terrestrial plants and weathering of clay rich soils and bedrocks contribute substantial amounts of organic and inorganic materials to river systems. These organics and clay particles, transported by the rivers, are discharged into the lagoons and estuaries.

Aggregation and flocculation of variety of organic matter and clay minerals that are transported by the rivers take place upon mixing with saline water in the marine environments. The viscous behavior of these marine sediments is expected to be influenced by the amount of organic matter present. A suspension of flocculated clay and organic materials can be found at or near the sediment-water interface, as in cases of “fluid mud” [1, 3, 5]. Understanding the viscous behavior of this type of flocculated material is important in many applications of marine engineering such as remote acoustic sediment identification, prediction of the amount of impact and subsequent burial of objects in seafloors and others. In this study, the viscous behavior of the flocs, representing typical cohesive marine sediments is investigated.

II. Materials

Montmorillonite was obtained from Clay Mineral Society (Chantilly, VA) for the study. Ca-montmorillonite (STx-1) is a 2:1 phyllosilicate. The atomic structure of montmorillonite is composed of an octahedral sheet which is sandwiched between two tetrahedral sheets. These structures are called TOT (Tetrahedral-Octahedral-Tetrahedral) layers. Clay particles are made of several of these TOT layers. The space between the TOT layers is called the interlayer space. For dry clays the interlayer distance is about 1nm (van Olphen, 1977). In montmorillonite, normally, clay layers are negatively charged due to isomorphous substitution. These negative charges are balanced by the cations that occur in the interlayer. The cations that occupy the interlayer in Ca-montmorillonite are calcium. Guar gum, which is a high molecular weight polysaccharide, was used as the organic material that represents typical bacterial extracellular polysaccharide abundant in the marine environment. Guar gum was obtained from MP Biomedicals, The structure of guar gum consists of galactose and mannose units. Due to lack of any functional groups that contribute to any charge, guar gum is considered as a charge neutral polymer [2]. Atomic structures of Ca-montmorillonite and guar gum are shown in Fig. 1. Artificial sea salt was used to produce the saline solution with the salinity of 35 PSU which is typical to the estuarine and marine environments.

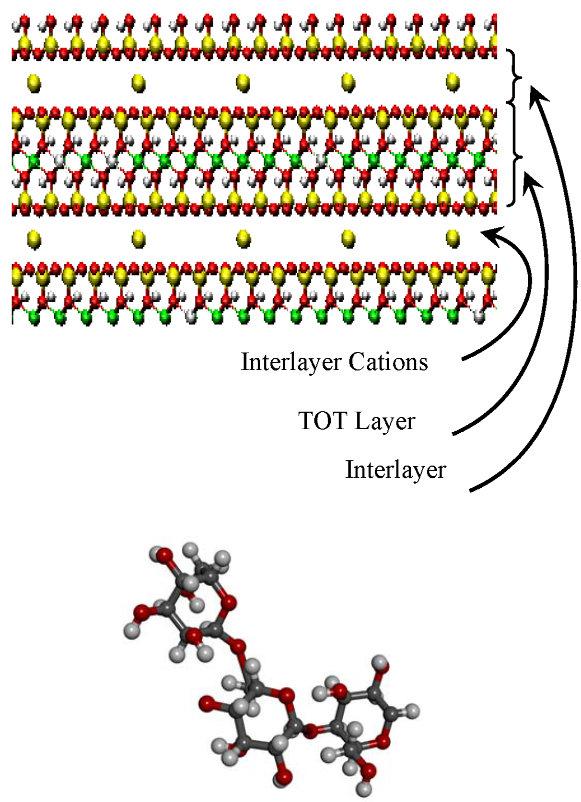

Fig. 1. Atomic structures of Ca-montmorillonite (top) and guar gum (bottom).

III. Methodology

A. Testing Equipment

A Brookfield R/S plus Rheometer with the double gap attachment DG3 DIN was used to test the viscosity of the floc suspensions. The "soft solid tester" (SST) configuration and the instrument data processing and analysis software (Rheo3000^{TM}) was used to calculate the viscosity and the shear stress measurements. The instrument is capable of measuring shear rates between 0.43 – 4340 1/sec and shear stress between 0.83 – 83 Pa. The nominal viscosity range is 0.19 mPa·s to 190 Pa·s. The filling volume of the measuring cup is 16 ml. The gap between the walls is 0.5 mm.

A Nikon Inverted Microscope, the *Eclipse Ti-S* version which is equipped with a camera and the Nikon image processing and analysis software, was used to perform the size analyses of the flocs. Four different objectives with 4X, 10X, 20X and 40X magnification lenses were used. The microscope slides that hold the floc suspensions for imaging were prepared by creating a 5 mm diameter hole on Plexiglas and mounting 0.25 mm thick glass slide

B. Preparation of Floc Suspensions

First, a suspension of Ca-montmorillonite clay particles of 2 micrometers and smaller were prepared by sedimentation column. Next, an appropriate amount of guar gum, which was pre-dissolved in water, was added to the clay suspension followed by addition of a concentrated saline solution to produce a mixture of target composition. 15 different floc suspensions were prepared by changing the clay/guar gum ratio. Constituents of these specimens are shown in the Table 1.

In a natural environment, the sedimentation of transported materials takes place when the river velocities are between 0.48 cm/sec and 30 cm/sec [4]. In order to mimic this natural environment, flocs were created by mixing the ingredients at a shear rate of 50 1/sec for 25 minutes in the double gap attachment of the Brookfield rheometer. This shear rate corresponds to the linear flow velocity of 2.1 cm/sec.

C. Measuring Viscosity

The study focuses on two main tasks. The first is to characterize the effect of clay/organic ratio on the viscosity of the floc suspensions. This was accomplished by changing the clay and the organic matter concentrations in the suspension. The percent organic content was changed as 0%, 1%, 3%, 4% and 5% of the clay concentration. The second goal of the study is to find out the effect of shear rate on the viscosity of the resulting floc suspensions. This was accomplished by conducting rheometer tests at several constant shear rate values: 250, 500, 750 and 1000 1/sec, which correspond to linear flow velocities of 11.7, 23.5, 35.2 and 46.9 cm/sec. The Brookfield R/S plus Rheometer instrument used in the study was calibrated using the Cannon viscosity standard N2 (Decane) to yield high accuracy results in the low-viscosity range for this instrument.

TABLE I. Constituents of the Floc Specimens

Sample No.	Clay g/L	Guar gum g/L	Salinity PSU
1-0-35	1	0.00	35
3-0-35	3	0.00	35
5-0-35	5	0.00	35
1-1-35	1	0.01	35
3-1-35	3	0.03	35
5-1-35	5	0.05	35
1-3-35	1	0.03	35
3-3-35	3	0.09	35
5-3-35	5	0.15	35
1-4-35	1	0.04	35
3-4-35	3	0.12	35
5-4-35	5	0.20	35
1-5-35	1	0.05	35
3-5-35	3	0.15	35
5-5-35	5	0.25	35

IV. Results and Discussion

A. Taylor and Reynolds Number Verification

In rotational viscosity testing, it is important to maintain the laminar flow conditions in the sheared suspension to ensure the validity of the values computed. Low viscosity fluids tend to reach the critical Taylor (T_a) and Reynolds (R_e) numbers relatively quickly with increasing shear rates in case when the inner cylinder of the rheometer is rotating and the outer one is stationary due to induced flow instabilities. Taylor and Reynolds numbers were calculated for all the specimens at each shear rate. It was found that the Taylor and Reynolds numbers do not reach their respective critical values in any of the viscosity tests conducted. TABLE II. shows the results of the critical value calculations for the two numbers at several shear rates used in experiments. The calculated values for R_e and T_a numbers are shown for the two fluids – water and a suspension of the lowest viscosity tested (as most critical) – all are within acceptable limits.

TABLE II. The Taylor and the Reynolds numbers for water and 1-0-35 floc specimen ons

Shear rate	250 (1/sec)		500 (1/sec)		750 (1/sec)		1000 (1/sec)	
T_a & R_e number	T_a	R_e	T_a	R_e	T_a	R_e	T_a	R_e
Water	25.8	167.1	28.4	184.1	36.3	235.5	45.0	291.6
1-0-35 sample	20.4	132.1	23.5	152.1	31.4	203.4	39.7	257.4

B. Viscosity of floc Suspensions

It was found that the increasing salinity up to 35 PSU (Practical Salinity Units) facilitates the formation of flocs for a given clay/guar gum concentration. Size comparison of the flocs for the specimens 1-5-35 and 5-5-35 are shown in Fig. 2. The flocs are larger and appear denser in the 5-5-35 specimen compared to the 1-5-35 specimen due to higher clay and guar gum concentrations.

Fig. 3 shows the effect of clay and organic matter content on the viscosity of the floc suspensions. In the figure, (a), (b) and (c) represent the viscosities of the suspensions prepared using 1, 3 and 5 g/L clay concentrations respectively. The organic matter content varies from 0% to 5% relative to the clay content in each set. It is observed that the increasing amount of organic matter results in significantly higher viscosity values in the suspensions. The results indicate that the higher the clay concentration of the specimen, the higher is the viscosity measured. This observation can be attributed to the greater amount of material present, naturally increasing the overall viscosity of the suspensions, and also to the larger and denser flocs that can be seen in these specimens.

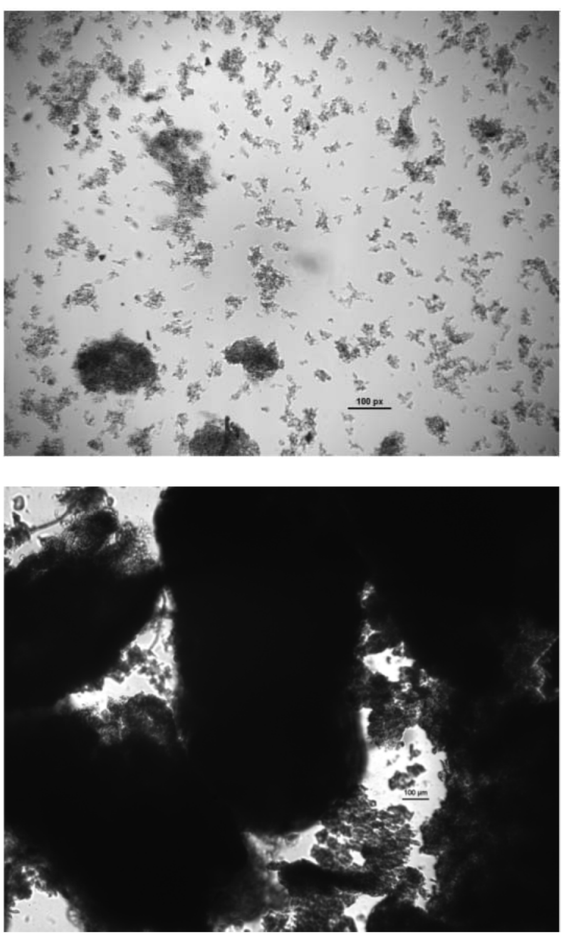

Fig. 2. Comparison of the flocs created using the specimens 1-5-35 (top) and 5-5-35 (bottom).

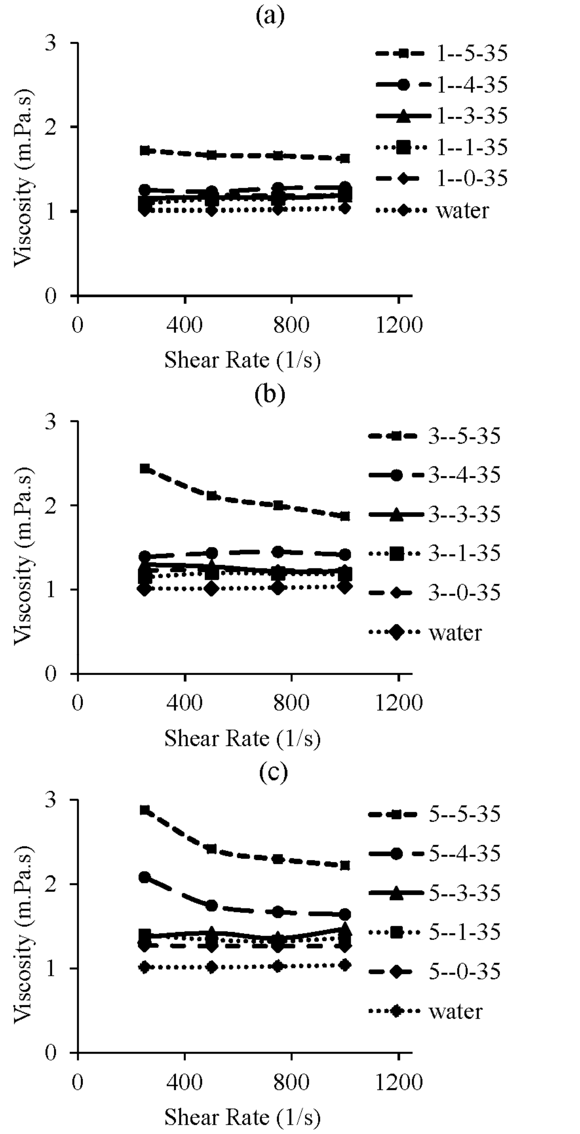

Fig. 3. Effect of the clay/organic matter content on the viscosity of the floc suspensions. (a), (b) and (c) are the floc suspensions containing 1, 3and 5 g/L clay concentrations respectively.

Relative viscosity of the floc suspensions were calculated as the ratio between the viscosity of floc specimens and the viscosity of water at a given shear rate. Fig. 4 shows the relative viscosity values of the specimens. In this figure, from (a) to (e) are the specimens containing 0, 1, 3, 4 and 5 % organic matter relative to clay. It is seen that the contribution of the clay fraction to the viscosity is insignificant when there is no organic matter present in the suspensions. The highest viscosity is observed when the organic matter content is 5% of the clay concentration. That indicates that the organic matter plays a major role in the viscosity of the floc suspensions. The samples with high clay/guar gum concentrations exhibit slight shear thinning behavior due to breakdown of the lager flocs into smaller flocs under high shear rates (Fig. 5).

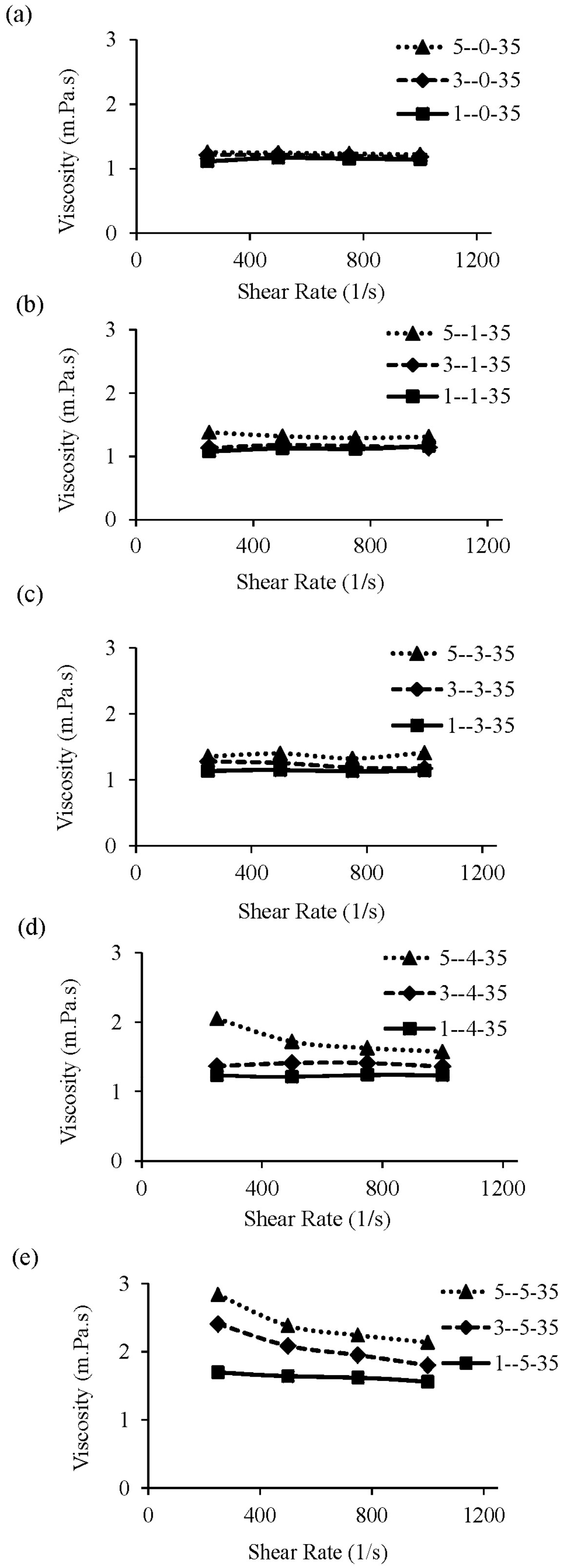

Fig. 4. Relative viscosity values of the specimens.

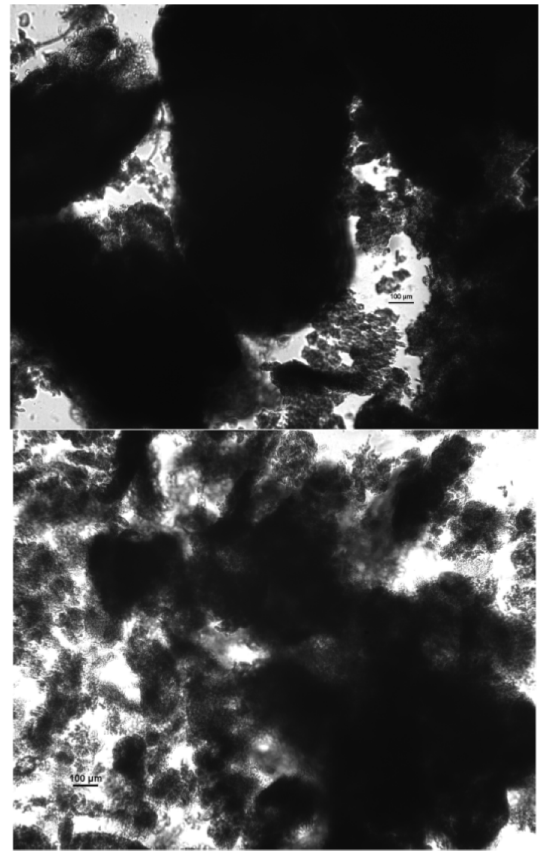

Fig. 5. Change in the size and the morphology of the flocs before (top) and after (bottom) applying 1000 1/sec shear rate for the 5-5-35 floc specimen

Most floc specimens tested exhibit Newtonian behavior within the shear rate range used in this study. Fig. 6 shows the relationship between the shear stress and the shear rate for the suspensions made using 5 g/L clay concentration. The linear regression that fits the results of water is also shown in the figure. A slight shear thinning behavior can be observed in the floc specimens with higher clay and organic matter, whereas for the very low OM concentrations, very slight shear-thickening effects could be observed at high (5 g/L) clay concentrations and only at higher shear rates. The change in behavior from mostly Newtonian to slightly shear-thinning may be occurring at OM concentrations of approximately between 3 and 4% OM, depending on the clay concentration. At the lowest clay concentration of 1 g/L, this effect is essentially not present, with all suspensions behaving as mostly Newtonian fluids.

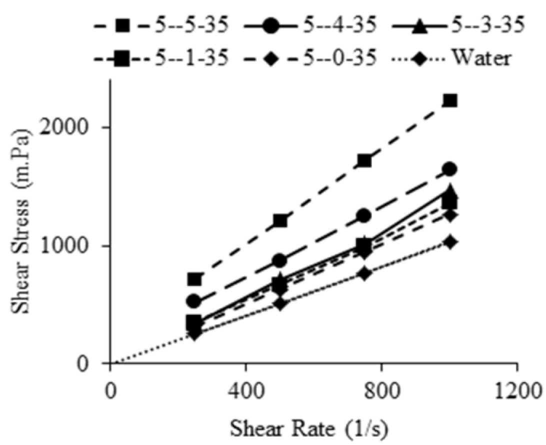

Fig. 6. Shear stress vs. shear rate relationship for suspensions with 5 g/L clay concentration.

C. *Empirical Equation for Viscosity*

Using the experimental data, an empirical equation (Eq. 1) was developed to describe the relationship between the viscosity, clay and the guar gum concentrations and the shear rates. In this equation, η, C, OM and CSR are the viscosity, concentration of clay, % organic matter content relative to clay, and the shear rate respectively. a_{ij} and b_{ij} are the constants that depend on the concentration of clay (i) and the shear rate (j). Values of the constants a_{ij} and b_{ij} are determined for the range of testing conditions and constituents.

$$\eta = C + a_{ij}\,(OM)^{5} + b_{ij}\,CSR \qquad (1)$$

The relationship between the constants (a_{ij} and b_{ij}) and the concentration of clay, C is illustrated in Figs. 7 and 8. Within the ranges tested, the data can be fitted with second degree polynomial functions.

Variation of viscosity with respect to % organic matter content relative to clay and, the shear rate. Red, green and blue are the measured viscosity for the specimens with 5, 3 and 1 g/L clay concentrations respectively. Grays are the corresponding fitted curves.

V. Summary and Conclusions

Flocculated suspensions of clay, organic matter and salt were prepared artificially by mixing Ca-montmorillonite, guar gum and sea salt. Fifteen different samples of different concentrations of flocs were prepared by changing the clay/guar gum ratio. Size and the morphology of these focs were examined by performing microscopic imaging. The viscosity of these floc samples were determined by imposing shear forces with four different shear rates from 250 to 1000 1/sec. It was found that presence of organic materials changes the viscous behavior of clay suspensions significantly. The higher the guar gum content the higher is the viscosity of the floc suspensions. It was also found that the floc suspensions which have higher clay and guar gum contents exhibit slight shear thinning behavior, especially above approximately 3-4% OM content for the highest clay concentration tested. This behavior was not observed at lower OM and clay concentrations. In fact, a very slight opposite (shear-thickening) effects could be seen at 1 and 3% OM (at 5g/L clay concentration). At lower clay concentrations, these effects are diminished and at clay concentration = 1 g/L, they are not noticeable with all the suspensions behaving in essentially Newtonian manner. It also was observed the larger and denser flocs tend to break down to smaller flocs during application of high shear rates. Using experimental viscosity results, an empirical model was developed. This model can be used to calculate the viscosity of a floc suspension when clay content, organic matter content and the shear rate are known.

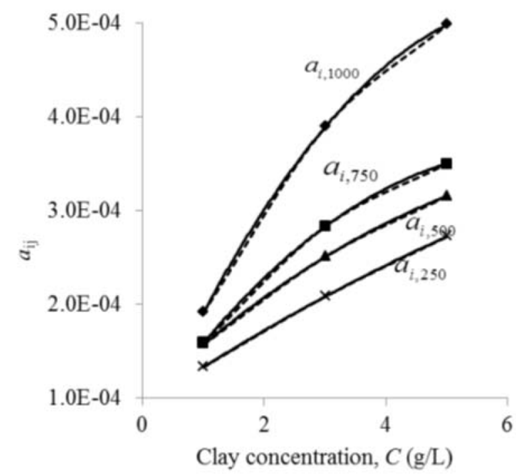

Fig. 7. Graph of clay concentration vs. constant a_{ij}.

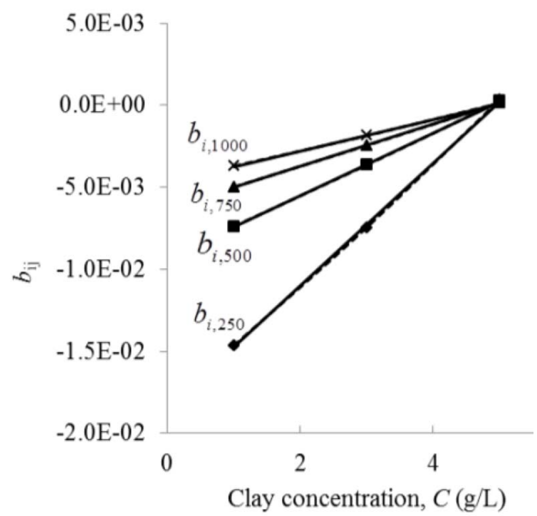

Fig. 8. Graph of clay concentration vs. constant b_{ij}.

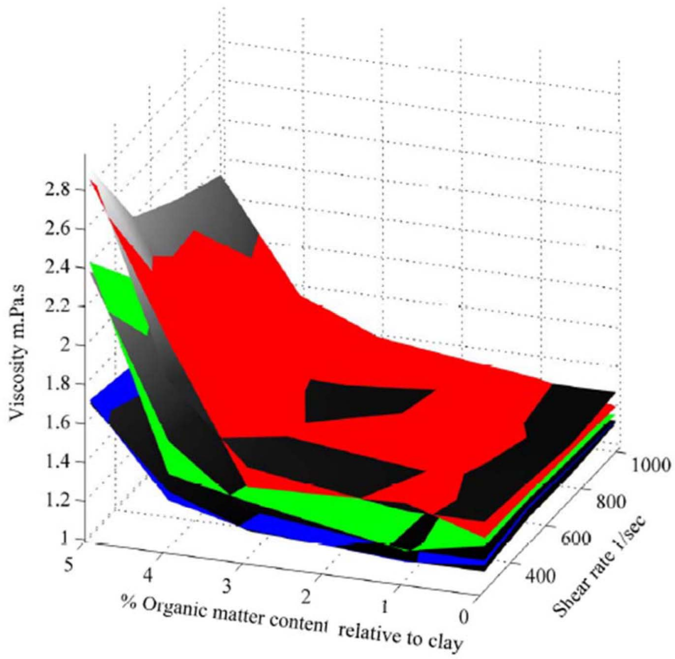

Fig. 9. Variation of viscosity with respect to the % organic matter and the shear rate.

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