Rheological properties of extracted oil from sludge

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ABSTRACT

Oily sludge is a viscous complex mix of hydrocarbons, water, metals, and suspended fine solids. This by-product's persistent toxic composition poses serious environmental concerns, making its containment one of the biggest challenges facing petroleum industries. The main objective of this research is to study the rheological properties of extracted oil. Petroleum sludge is considered a non-Newtonian fluid. However, after the application of Electro-Kinetic phenomena, demulsification of the matrix took place, and separated phases started expressing different behaviours. The diffuse double layer of the sludge components, particularly those known as emulsifiers (e.g. asphaltenes, and resins), were affected by DC field. Since they were affected in different ways, the separation of phases was facilitated, where each component expressed different physicochemical properties (including viscosity, and shear rate). Accordingly, the measurement of rheological properties permitted to follow adequately the changes observed in the oil matrix. Then, viscosity was measured as a function of strain at the top, middle, and bottom areas of the anode, cathode and central areas. However, the elastic modulus, which is a measure of the stiffness of the sludge, was presented as a function of frequency for the same areas. It can be concluded, that the EK (Electro-Kinetic) remediation directly affects the rheological properties of the sludge, by targeting the microstructure of the sludge. Disturbing the thermodynamically stable system, and affect the energy barrier (resultant of the attractive and repulsive forces), which prevents particles from coalescence. It seems that DC field affected the zeta potential of the system, by changing the balance of ions in the diffuse double layer. It is visible particularly in the presence of high Conductive metals.

Key words: Electro-Kinetic, oily sludge, viscosity, rheological properties

INTRODUCTION

One out of major challenges facing the petroleum industry today is finding an acceptable and cost-effective solution, to manage the growing amounts of oily sludge, generated through the upstream, midstream, and downstream sectors of this industry. The latter sectors refer respectively to the extraction and production, storing, and transporting petroleum crude oil, and finally refining and treating of oil. Oily sludge belongs to a multi-component system, mainly characterized as an oil-in-water, or water- in-oil systems, mixed with suspended solids. This homogeneous viscous mix is usually in full emulsification.

J.C. Baudez et al. shows that the rheological properties of municipal anaerobic digested sludge rheology are temperature dependent. It was shown that both solid and liquid characteristics decrease with temperature. On the other hand, the yield stress and the high shear (Bingham) viscosity are the two key parameters determining the rheological behaviour. By normalizing the shear stress with the yield stress and the shear rate with the yield stress divided by the Bingham viscosity, a master curve was obtained, independent of both temperature and concentration. The rheological behaviour is irreversibly altered by the thermal history. Dissolution of some of the solids may cause a decrease of the yield stress and an increase of the Bingham viscosity. The usual laws used to describe the thermal evolution of the rheological behaviour of fluids are no longer valid with anaerobic digested sludge. Finally, the impact of temperature and thermal history have to be taken into account for the design of engineering hydrodynamic processes such as mixing and pumping [6].

Rheology is very crucial to study the behavior of complex material. Previous studies showed the rheological properties of complex fluid in micropump [1, 4]. Many studies of high viscous liquids using macro screw pump were performed by D.W.Cooper [2]. He was dealing with spills of viscous oils, and particularly spills in cold climate. However, the results for pumping the bitumen were inconclusive. From an engineering standpoint, sludge consists of natural soil which presents a medium that is complex in structure, physic-chemical properties and general behavior. Knowledge of the soil horizon forms the initial foundation for the study of soil composition. The efficiency of any remediation effort is predicated on a knowledge of soil composition, since this presents an idea related to the fate (transport, transformation and remediation) [5]. Therefore the objective of this paper is to study the rheological properties such as viscosity, elasticity,…etc. of oily sludge.

J.C. Baudez et al. determined the rheological behaviour of digested sludge at different concentrations, and highlighted common features. At low shear stress, digested sludge behaves as a linear viscoelastic solid, but shear banding can occur and modify the apparent behaviour. At very high shear stress, the behaviour fits well to the Bingham model. Finally, the rheological behaviour of digested sludge is qualitatively the same at different solids concentrations, and depends only on the yield stress and Bingham viscosity, both parameters being closely linked to the solids concentration [7].

NOMENCLATURE

K	[Pa.s]	the sludge flow consistency index
γ	[1/s]	the strain rate
n		the dimensionless flow behavior index
τ	[Pa]	the shear stress
μ	[Pa.s]	the dynamic viscosity
γ	[1/s]	the strain rate

Methodology

Figure 1 summarizes the methodological approach

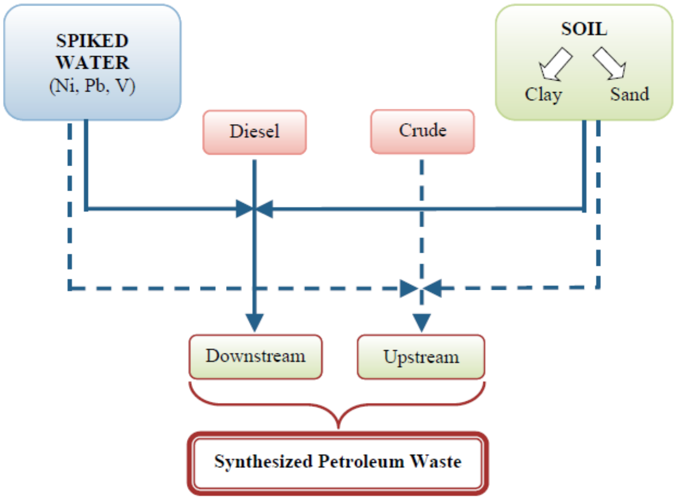

Figure 1 Methodological approach for sludge preparation

Rheological properties in this research were measured by an MCR500 rheometer Fig (2) which was manufactured at Physica company. It was used to better understand the science behind the deformation and flow of upstream and downstream sludge samples. A plate/plate measuring system Fig (3) was used for this purpose.

Figure 2 MCR 500 Rheometer

Figure 3 Plate/plate measuring system.

To analyse the results generated from the test, Rheolplus /32 version 3.40 software was used. This software is provided with the device and it was developed by the German company Anton Paar.

Results

Upstream oily sludge matrix

Figure 4 shows the viscosity changes with respect to the strain rate in the upstream control cell. Viscosity was decreasing while increasing the strain rate. When the strain rate reached 6 1/s the viscosity had insignificant changes afterward.

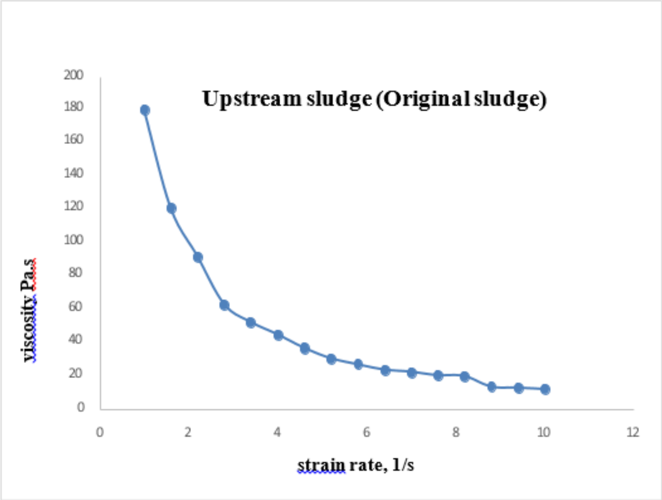

Figure 4. Viscosity of the upstream Control Cell (initial oily sludge matrix) as a function of the strain Note: Original Cell: oily sludge matrix not exposed to DC (direct current) field

Rheological properties of the upstream/downstream Vanadium Cell

Figures 5 to 9 describe the changes in viscosity at the bottom areas of the cell. These areas are considered more important when it comes to rheological properties, since bottom areas accumulated higher amounts of the solid sludge than the top parts, where the liquids had accumulated. The precipitated fractions of oily sludge usually contain emulsifiers, such as asphaltene, where the polar fraction of this compound has been found to contain relatively high amounts of vanadium and nickel.

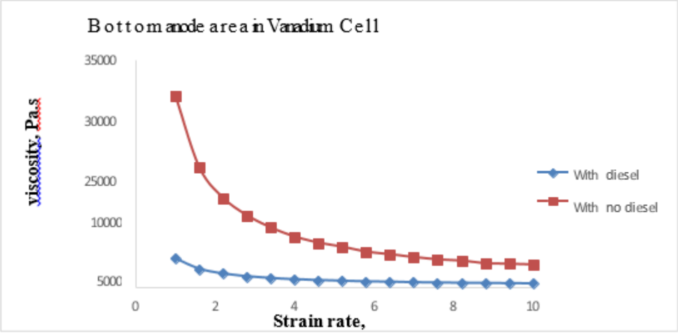

Figure 5. Viscosity of the bottom anode sludge as a function of the strain rate

Figures (6, 7, and 8) show that the viscosity was constant while increasing the strain rate, for the cathode and center samples, either with diesel or without diesel. It also reveals that diesel did not affect the samples rheological properties. On the other hand, in the bottom anode area (Fig 5) of the upstream sludge matrix (without diesel), the viscosity decreased while increasing the strain rate, but downstream, a slight changes with increasing the strain rate were to be seen due to the microstructure changes.

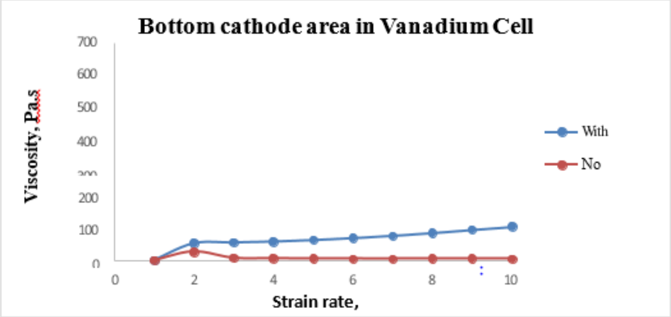

Figure 6 Viscosity of the bottom cathode sludge as a function of the strain rate

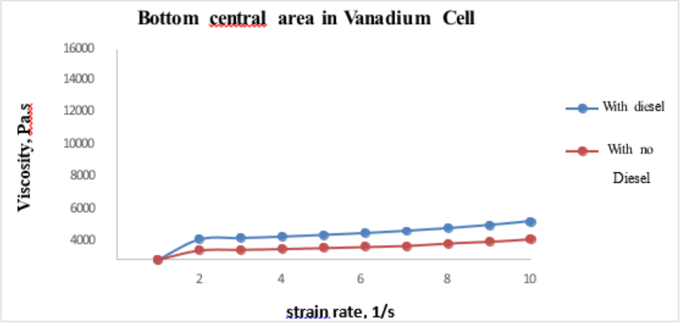

Figure 7. Viscosity of the bottom central area sludge as a function of the strain rate

Figure 8 shows that the bottom anode has a higher storage modulus than the cathode and center areas.

The storage modulus for bottom center sample was high when compared to the bottom cathode. However samples from the anode had the highest storage modulus. Due to a possible experimental error, bottom cathode curve was not a straight line. Also we can observe that elastic modulus is independent of frequency.

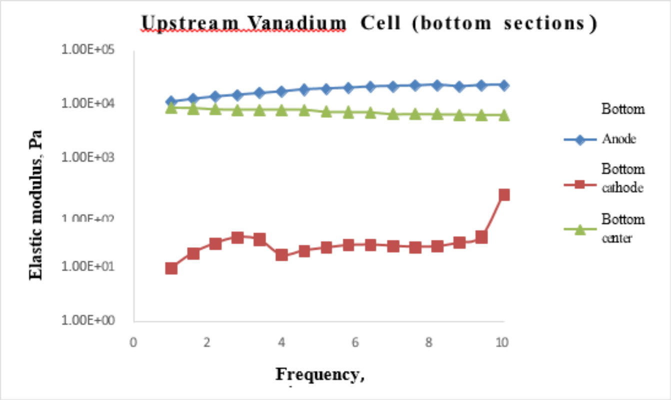

Figure 8 Elastic modulus as a function of frequency for bottom anode, cathode and center upstream Vanadium Cell

Figure 9 illustrate the storage or elastic modulus as a function of frequency for bottom anode, cathode and center samples in the downstream cell (with diesel). It was obvious that the bottom center samples had very high elastic modulus. The bottom cathode had lower elastic modulus than the anode. In all samples the elastic modulus is constant with the frequency.

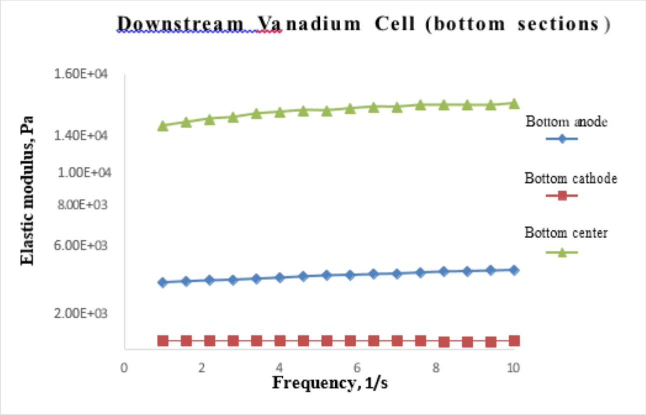

Figure 9 Elastic modulus as a function of frequency for bottom anode, cathode and center downstream Vanadium Cell

Figure 10 describes the changes in viscosity of the top anode, cathode and center upstream samples with respect to strain rate. The figure shows that the viscosity is constant with increase of strain rate at the top cathode area. However, top of the anode sample has much higher viscosity than top of the cathode and center. When the strain rate reached 10 1/s the viscosity reached 15000 Pa.s

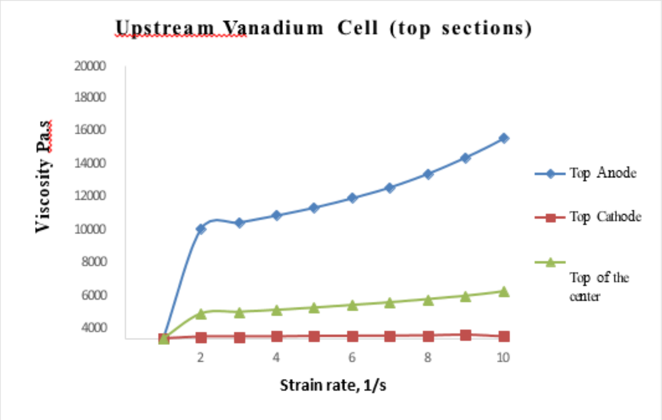

Figure 10 Viscosity as a function of strain for top anode, cathode and center samples

It can be concluded, that the EK remediation directly affects the rheological properties of the sludge, by targeting the microstructure of the sludge. Disturbing the thermodynamically stable system, and affect the energy barrier (resultant of the attractive and repulsive forces), which prevents particles from coalescence. It seems that DC field affected the zeta potential of the system, by changing the balance of ions in the diffuse double layer. It is visible particularly in the presence of high conductive metals.

Thus, the highest and fastest demulsification was observed in presence of vanadium. In fact, the term "electro-rheology" phenomena could be used, which lead to change of matrix properties and appearance of distinctive phases, in various parts of the cells. For example Figures 5, and 10 illustrate higher viscosity with respect to strain rate at the anode in Vanadium Cell, comparing to the center and cathode areas.

Such viscosity increase is directly related to the increase of zeta potential, and the drop of pH. By the end of the experiment, stable separated fractions demonstrated characteristics such as, low pH values at the anode, high pH values at the cathode, high viscosity at the anode, and low viscosity at the cathode, indicating an excellent separation of phases that took place after the electro-demulsification of the oily sludge matrix.

From visual observations, pH values and characterization of the sludge, Nickel and Lead Cells showed generally similar characteristics of that in Vanadium Cell. Therefore a simple rheological model was implemented depending on Figures 5.38 and 5.39, where the viscosity "μ" (as a function of rate of strain) is decreasing in what is referred to as shear is thinning. The best rheological model that could fit such behavior was found to be Ostwald –de Waele-power model:

$$\mu = K(\gamma)^{n-1} \qquad (1)$$

Where:

K: is the sludge flow consistency index (Pa.s), γ is the strain rate (1/s), and n is the dimensionless flow behavior index (in these results it is negative because the flow is shear thinning, n = -0.944).

However, Figures 6 to 10 viscosity seemed to be mostly independent of the rate of strain, therefore the best rheological model fit these figures is the Newton model:

$$\tau = \mu \gamma \qquad (2)$$

Where:

τ : is the shear stress (Pa), μ: is the dynamic viscosity (Pa.s), and γ : is the strain rate (1/s)

Experimental investigation

Tests were conducted on laboratory-prepared contaminated samples to assess SFE extraction efficiency of phenanthrene from clayey soils. They were performed on pure materials, namely kaolinite, illite, and montmorillonite, and sandy soils with different illite content.

Materials

In this investigation four commercial materials were used: kaolinite, illite, montmorillonite, and pure silica sand (0.06–0.2 mm). The samples consisted of pure kaolinite, illite, andmont- morillonite, and mixtures of illite and fine pure silicasand (S_4 : 60% illite and 40% sand; S_5 : 50% illite and 50%sand; S_6 : 20% illite and 80% sand; and S_7 : 100% sand). They were prepared to simulate various site conditions (i.e., dry and wet conditions). All samples were contaminated with phenanthrene to a concentration level of 200 mg/kg of dry soil.

Conclusion

The objective of this research is to study the effect of Vanadium on the properties of sludge. Ten different samples have been carried out, bottom anode area in Vanadium cell with diesel and without diesel, bottom cathode area in Vanadium cell with diesel and without diesel, bottom of center area in Vanadium cell with diesel and without diesel, top anode area in Vanadium cell without diesel, top cathode area in Vanadium cell without diesel, top of the center area in Vanadium cell with no diesel and the upstream sludge (control or original cell). It can be concluded, that the EK remediation directly affects the rheological properties of the sludge, by targeting the microstructure of the sludge. The viscosity decreases with increasing the strain without adding diesel. However, elastic modulus doesn't change with increasing the frequency. In the future, more rheological tests (yield stress, thixotropy) will be studied, the current rheometer can't be used to study these properties.

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