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PRELIMINARY STUDY OF LOCAL BENTONITE TREATMENTS FOR OIL AND GAS INDUSTRY

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Bentonite, treatment, ion exchange, additive

ABSTRACT

Bentonite was the first material used extensively as an additive in oil and gas industry especially in drilling mud and oilwell cement. In order to reduce the overall cost in oilwell drilling and completion, the development of local bentonite has been initiated. The samples of this study were taken from the areas of Lahad Datu and Tawau, Sabah, East Malaysia. As the local bentonite is not a sodium-based, a treatment method is sought to replace some of the ions on the unit clay surfaces with sodium ions. In this study, two methods were suggested for the purpose of ion exchange, the first being the wet method. In wet method, sodium carbonate, sodium bicarbonate or sodium chloride is used as the source of sodium ions. The process must be run in wet condition, that is either in solution form or in high moisture condition. The other method is the electrolysis process, in which an electric current will be used to perform the required ion exchange process. Before and after treatments, the local bentonite samples will be tested for physical and chemical properties, and mineral content to determine the optimum condition for the treatment processes, as per the API Specification 13A, 10A and OCMA requirements. Subsequently, tests will be run for the treated local bentonite in such applications as drilling mud (water-based mud), and oilwell cement slurry compare with the performance of commercial Wyoming bentonite.

INTRODUCTION

Bentonite is a clay with montmorillonite as its main mineral. It has many application in various industries, such as drilling mud and cement additives, to decolorize oils, fats and greases, ceramic material, foundry molding and iron pellets. The use of bentonite depends on their properties; hence it is desirable to consider uses and properties together. The properties of bentonite are contingent upon the fact that they are composed of smectite clay minerals, and the properties of the smectite in turn are contingent upon its chemical composition, atomic structure, and morphology. Due to all foregoing characteristics, some properties of bentonites will vary from sample to sample even in a given deposit. The cation exchange capacity (CEC) of clay minerals, which may presence in bentonite is showed in Table I.

The commonly used bentonite consists of sodium ions instead of calcium ions placed between the unit clay surfaces as the counter ions. The type of counter ions has a great effect on the swelling capacity of the montmorilonite and by far the best performance is obtained with sodium montmorilonite, which has sodium

as counter ions. If the montmorilonite contains counter ions other than sodium, the swelling properties, viscosity build-up and filter cake permeability will be adversely affected especially when the bentonite is used in drilling fluids. Table II shows the API 13A and OCMA requirements for bentonite to be used as an additive to drilling mud and Table III shows the API Specification for bentonite usage as an oilwell cement additive. For example, the good bentonite gives a lightweight cementing system, good fluid loss control, good rheological properties and adequate compressive strengths.

There are many types of clay minerals, the most important types of minerals are: illite, kaolinite, attapulgites, chlorites and smectite. One of the member of smectite groups is montmorillonite, and also called Na-bentonite. Na-bentonite has an expanding lattice, where all layers surface are available for hydration and cation exchange. Na-bentonite structure is classified as dioctahedral, having two thirds of the octahedral sites occupied by trivalent cations.

The important characteristic of bentonite minerals are able to provide in such applications is adequate particle dispersion, which is necessary to obtain a uniform and stable system. There are two types of bentonite, Ca-bentonite and Na-bentonite. The commonly used in oil and gas industry is Na-bentonite, because it has high plasticity and can absorb a large amount of water. But most of Malaysian bentonite consist of Ca-bentonite and a lot of impurities. That is why an appropriate treatment should be carried out to improve bentonite quality. One of the approach is by cation exchange, it means calcium based will be exchanged by sodium based. The treatment processes will be used in this study are wet treatment process and electrolysis process.

RESEARCH METHODOLOGY

Field Sampling

In this research, two groups of local bentonite samples were collected, namely SA5 (N4⁰18.97'- E 117⁰57.37') from Andrassy area in Tawau district and M4 (N5⁰7.35'- E118⁰ 12.03') from Mansuli area in Lahad Datu district. The sample was collected exactly at 0.5 m depths for Andressy and Mansuli at 0.3 m. The field sampling from Mansuli area were taken mainly in area underlain by the Ayer Formation, which collectively form the Segama Group and is interpreted to be Miocene in age (Khairuddin & Radzuan, 1992). The Ayer Formation has two distinction lithofacies; the bedded tuffaceous facies comprising bedded tuff, tuffaceous sediment, and volcanic breccias and the polymict boulder-bed facies comprising slump brecia. An additional lithofacies is the calcareous facies comparising the Tempadong Limestone Member, which is believed to occur as massive lenses within the bedded tuffaceous facies (Godwin, 1994). The Andrassy area is underlain mainly by the high level of alluvium and volcanic rock, and occur in a bed underlying by Pleistocene to Holocene in age. (Yusairi & Yan, 1995)

Bentonite Sample Preparation

Local bentonite samples from the field will be dried in the oven at 55 °C for four hours until reach moisture content less than 10%. Then the sample will be crushed using grinding machine till it become powder. Selection of bentonite grain size is very important to obtain optimum cation exchange. Based on literature (API specification 13A, 1985), showed that sand grain size is bigger than 74 μ m, so the bentonite that will be used for this treatment should be less than 74 μ m. To produce bentonite powder with grain size less than 74 μ m, wire cloth sieve will be used for sieving process.

Physical and Chemical Properties Determination

Commonly, the chemical property of bentonite is cation exchange capacity (CEC). Meanwhile, the physical properties determination include the Atterberg limit such as liquid limit (LL), plastic limit (PL) and plasticity index (PI), moisture absorption (MA), moisture content (MC) and ignition loss (IL). Methylene Blue Test (MBT) is used to estimate the cation exchange capacity. In Table I, a sodium-based bentonite should have a CEC value same as that of montmorillonite. Approximately 1 gram of bentonite sample will be tested in 50 ml of distilled with about 0.5 ml of 5 N sulfuric acid added. The bentonite

solution will than boiled gently for 10 minutes. The CEC is measured by conductomercial titration after cation exchange. The exchanged cation will be measured in meq/100grams.

The physical study values are used to obtain information on the nature and quality of the mineral by using Atterberg Limits Test, such as plastic limit (PL), liquid limit (LL) and plasticity index (PI). The standard testing method for liquid and plastic limit according to ASTM specification is ASTM 4318-84. Liquid limit and plastic limit also refer as Atterberg limit, which depending on the moisture content of bentonite sample. The liquid limit provides the moisture content at which the clay changes from plastic to the liquid state. While the plastic limit was simply the moisture content at which a ball of clay when rolled to a diameter of 1/8 inch. On the other hand, plasticity index is the difference between liquid limit and plastic limit. In addition, the moisture adsorption (MA), moisture content (MC) and ignition loss (IL) of bentonite will also be determined since the qualitative mineral content of bentonite can be studied. Moisture adsorption (MA) is defined as the percentage of water lost when clay from a saturated atmosphere (around 20°C) is dried in an oven at 105°C. The moisture adsorption value can be used to predict the mineralogy nature for clay. Moisture content (MC) is the percentage of water lost when clay from normal room temperature atmosphere (at around 20°C) is dried at 105°C. While the ignition loss is the percentage of weight lost when a dried clay (at 105°C) is fired to 1000°C in furnace.

Wet Treatment Process

The most common wet treatment process is mixing the calcium-based bentonite directly with the solution that contains sodium ions as the exchange medium. The entire treatment process need to be run under the wet condition, that is either in solution form or in high moisture condition. The additive used in wet treatment process is chemicals that contain sodium ion such as sodium carbonate (soda ash), sodium chloride (salt), sodium bicarbonate and sodium hydroxide (caustic soda). First, mixed an additive with fresh water to form a sodium ion solution. This solution will then blended with bentonite sample to form a bentonite solution or paste-like semisolid. The mixture will then left for a few days or longer to ensure that the ion exchange can react effectively. The reaction will be as following equation;

Electrolysis Treatment Process

The electrode and tank are accurately prepared to provide similar boundary condition. The experiment will be applied by putting electrode inside the solution of bentonite slurry and NaCl as an electrolyte. The direct current will be passed through the electrode. The positive ions migrate to the negative electrode and the negative ions migrate to the positive electrode. At the negative electrode each positive ion gains an electron and becomes neutral; at the positive electrode each negative ion gives up an electron and becomes neutral. The technique chosen for this system is the "inert electrode", because the solid surface of the cathode hold a role of providing the surface for reaction and not involved in the reaction.

The experiment will be carried out at the room temperature and atmospheric pressure. The variable parameters are voltage, times, bentonite concentration and NaCl concentration.

This electrolysis treatment will be run as follows:

$$2\text{NaCl}(aq) \longrightarrow 2\text{Na}^{+}(aq) + 2\text{Cl}^{-}(aq)$$

$$2\text{H}_{2}\text{O} + 2\text{e} \longrightarrow 2\text{OH}^{-}(aq) + \text{H}_{2}(g)$$

$$2\text{Cl}^{-}(aq) \longrightarrow \text{Cl}_{2}(g) + 2\text{e}$$

$$2\text{NaCl}(aq) + 2\text{H}_{2}\text{O} \longrightarrow 2\text{NaOH}(aq) + \text{H}_{2}(g) + \text{Cl}_{2}(g) \qquad (3-2)$$

After Ca-bentonite (Ca-X) and other mineral content in bentonite (M-X) placed in the solution, it will disperse into its ion and the reaction follows the following equation:

| $CaX \longrightarrow Ca^{++} + X^{2-}$ | (3-3) |
|--|-------|
| MX — M ⁺ + X ⁻ | (3-4) |
| And the final reaction from equations 3-2 and 3-3 will produce Na-bentonite, in the formula: | (3-4) |
| $2Na^+ + X^2 \longrightarrow Na_2X$ | (3-5) |

Performance Tests as a Drilling Mud Additive

The requirement of bentonite in drilling mud is based on API 13A and OCMA specifications (API Spec. 13A, 1985). The suspension properties of bentonite sample will be tested using the Fann rheometer, which give us the important suspension properties of drilling mud. From the reading taken, plastic viscosity (dial reading 600 rpm – 300 rpm) and the yield point (plastic viscosity – dial reading 300 rpm) of drilling mud can be determined. For fluid loss property, a low pressure, low temperature filter press can be used.

Performance Tests as an Oilwell Cement Additive

The specification of oilwell cement using bentonite is based on API Specification 10A (API Spec. 10A, 1995). For oilwell cement testing as mentioned in API Specification 10A only free water testing is needed which poured the cement slurry with bentonite added into 250 ml cylinder glass and let it suspended for two hours.

RESULTS AND DISCUSSION

Cation Exchange Capacity

Table IV indicates that the cation exchange capacity (CEC) of untreated local bentonites of M4 and SA5, which were 21 meq/100 grams and 41 meq/100 grams, respectively. These are very low compared with that of montmorillonite, which was 80 - 150 meq/100 grams.

Liquid Limit, Plastic Limit and Plasticity Index

The results of liquid limit, plastic limit and plasticity index is showed in Table V. From the chart plastic limit versus plasticity index (Bain, 1971), bentonite samples of M4 and SA5 fall within the plastic kaolin category, which was near to the calcium based montmorillonite area. Meanwhile, standard bentonite fall within the sodium based montmorillonite area, which as expected.

Moisture Adsorption and Ignition Loss

Moisture absorption of bentonite is the indicator to determine the mineral content qualitatively. From Table VI, the MA of M4 and SA5 values are lower than 23% (Moreira, 1984), which are 9.51% and 11.91% respectively, this mean the bentonite samples contains some impurities other than montmorillonite mineral such as kaolinite, illite and chlorite. For bentonite with MA value more than 23%, the sample should contains about 80% of montmorillonite mineral, with some other minor impurities. Ignition loss value indicated the ability of bentonite to absorb a specified amount of water, it means sodiumbased bentonite will have a higher value of ignition loss as compared to untreated local bentonite.

Performance as an Additive in Drilling Mud

From Table VII, when the untreated local bentonite was used as an additive in drilling mud, the suspension properties of the drilling mud almost failed to meet the API and OCMA requirements. For M4 and SA5 samples, the viscosities recorded were substantially lower than the standard values, despite having favorable yield point over plastic viscosity ratios. However, the moisture content of both samples fulfilled the API and OCMA requirements. No gelling effects were observed for the drilling mud prepared using untreated local bentonites. The tests also revealed the very high filtrate volumes given by the bentonite samples of M4 and SA5.

Performance as an Additive in Oilwell Cement

The performance of untreated local bentonite before used as an additive in oilwell cement is shown in Table VIII. It is clear that the untreated local bentonite failed to satisfy any of the API 10A requirements as shown in Table IV. Not only the yield point over plastic viscosity ratio, the dispersed plastic viscosity was also very low. Further, the fluid loss recorded was much more higher for both bentonite samples compared to the standard requirement. In addition, the performance of cement slurry when bentonite is added should have a free water of 1.4%, as mentioned in API specification 10A. From Table IX, it can be seen that free water performance of M4 sample meets the API specification, but not for sample from SA5 area.

CONCLUSION

From the preliminary study, the untreated local bentonite can be categorized as low quality bentonite as compared to the standard bentonite. From the performance tests, the results were not very encouraging as the main properties of the drilling mud and cement formulated using untreated local bentonites were generally inferior to the standard properties. The overall quality of local bentonite can be improved by implementing the treatment process proposed in this paper.

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Table I: Cation Exchange Capacity of Clay Minerals (Grim, 1962)

| Mineral | CEC, meq/100 grams |
|------------------------------|--------------------|
| Kaolinite | 3 – 15 |
| Halloysite 2H ₂ O | 5 – 10 |
| Halloysite 4H ₂ O | 10 - 40 |
| Montmorillonite | 80 – 150 |
| Illite | 10 – 40 |
| Vermiculite | 100 – 150 |
| Chlorite | 10 – 40 |
| Sepiolite-Attapulgite | 20 – 30 |

Table II: API and OCMA Requirements for Bentonite as an Additive in Drilling Mud (API Spec. 13A, 1985)

| Requirement | API 13A specification | OCMA specification |
|--|-----------------------------------|-----------------------------------|
| Viscometer Dial Reading at 600 rpm | 30 cp, minimum | 30, minimum |
| Yield Point/Plastic Viscosity Ratio | 3, maximum | 6, maximum |
| Filtrate Volume | 15.0 cm ³ , maximum | 16.0 cm ³ , maximum |
| Moisture | 10.0 wt. percent, maximum | 13.0 wt. percent, maximum |

Table III: API Specification for Bentonite as an Oilwell Cement Additive (API Spec. 10A, 1995)

| Requirement | API Specification |
|--|-----------------------------------|
| Yield Point/Plastic Viscosity Ratio | 1.5, maximum |
| Dispersed Plastic Viscosity | 10 cp, minimum |
| Dispersed Filtrate Volume | 12.5 cm ³ , maximum |

Table IV: Cation Exchange Capacity of Untreated Local Bentonite

| Sample | CEC, meq/100 gram |
|--------|-------------------|
| M4 | 21 |
| SA5 | 41 |
| | |

Table V: Atterberg Limit Test of Untreated Local Bentonite

| Liquid Limit (LL) | Plastic Limit (PL) | Plasticity Index (PI) |
|-------------------|--------------------|-----------------------------|
| 80.7 % | 29.8% | 50.9% |
| 68.9% | 32.2% | 36.7% |
| 644.5% | 57.64% | 586.9% |
| | 80.7 % 68.9% | 80.7 % 29.8% 68.9% 32.2% |

TableVI: MA, and IL of Untreated Local Bentonite

| Sample | Moisture Adsorption (MA), % | Ignition Loss (IL), % | |
|--------------------|-----------------------------|-----------------------|--|
| M4 | 9.51 | 931 | |
| SA5 | 11.91 | 10.32 | |
| Standard Bentonite | 27.61 | 8.76 | |

Table VII: The Suspension Properties of Untreated Local Bentonite Used as an Additive in Drilling Mud.

| Requirement | Standard Bentonite | M4 | SAF |
|--|--------------------|------|-------|
| Viscometer Dial | 35 | 4.5 | SA5 |
| Reading at 600 rpm, cp | | ۷,۶ | 5 |
| Yield Point/Plastic Viscosity Ratio | 29 | 0.5 | 0.5 |
| Filtrate Volume, cm ³ | 14 | | |
| | 14 | >50 | >50 |
| Moisture, % | 13.43 | 4.88 | 10.62 |

Table VIII: The Suspension Properties of Untreated Local Bentonite Used as an Additive in Oilwell Cement.

| Requirement | Standard Bentonite | M4 | SA5 |
|---|--------------------|-----|-----|
| Yield Point/Plastic Viscosity Ratio | 29 | 0.5 | 0.5 |
| Dispersed Plastic - Viscosity, cp | 3 | 2.0 | 2.0 |
| Dispersed Filtrate Volume, cm ³ | 14 | >50 | >50 |

Table IX : The Free Water Performance when Untreated Local Bentonite Used as an Additive in Oilwell Cement.

| | · · · · · · · · · · · · · · · · · · · | | * | |
|---------------|---------------------------------------|------|--------|---|
| | Standard Bentonite | M4 | CAE | |
| Free Water, % | | 1717 | J/ SAS | |
| | 0.84 | 1.16 | 1 48 | |
| | | | 1.70 | 1 |