ELECTROLYSIS TREATMENT STUDY OF SABAH BENTONITE AND ITS APPLICATIONS IN PETROLEUM INDUSTRY

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ABSTRACT

Based on the result of Geological Survey Department Malaysia investigation, the bentonite resources in Sabah is great amount. In order to reduce the overall cost in oilwell drilling and completion, the development of Sabah bentonite as drilling mud material and oilwell cement additive has been initiated. In addition, Sabah bentonite is categorized as not sodium based bentonite. Appropriate treatement method is sought to replace some of the ions on the unit clay surfaces with sodium ions. One of the methods that proposed is electrolysis treatment method. There are two objectives that can be summarized in this study. The first one was to determine optimum electrolysis treatment. The result obtained after the treatment methods showed improvement in cation exchange capacity (CEC), which is about 27% increment of original CEC value. The higher CEC value indicates the improvement in water absorption capability of bentonite. The second objective was to determine the performance of bentonite as drilling mud material and oilwell cement additive compare with standard bentonite and API (American Petroleum Institute) Specification 13A and 10, respectively.

Keywords : bentonite, electrolysis treatment, cation exchange capacity, drilling mud material, oilwell cement additive

INTRODUCTION

Bentonite is a clay with montmorillonite as its main mineral. It has many application in various industries, such as in petroleum industry as drilling mud material and oilwell cement additives. Bentonite has an expanding lattice, where all layers surface are available for hydration and cation exchange. Bentonite structure is classified as dioctahedral, having two thirds of the octahedral sites occupied by trivalent cations. 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 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.

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 is electrolysis treatment process.

RESEARCH METHODOLOGY & EXPERIMENTAL WORK

Field Sampling

In this research, two groups of local bentonite samples were collected, namely SA51 and SA54 (N4^{0}18.97'- E 117^{0}57.37') from Andrassy area in Tawau district and M4 (N5^{0}7.35'- E118^{0} 12.03') from Mansuli area in Lahad Datu district. The SA51 sample was collected exactly at 0.5 m depths, SA54 sample was collected at 1.0 – 1.5 m depths and M4 at 0.3 m depths. 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.[7] 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.[12]

Bentonite Sample Preparation

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, 1993), showed that sand grain size is bigger than 74 μm, so the bentonite samples used for this treatment should be less than 74 μm, which can be achieved by using wire cloth sieve.

Physical and Chemical Properties Determination

Common chemical property of bentonite is CEC. In addition, 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 CEC. A sodium-based bentonite should have a CEC value same as that of montmorillonite (80 –10 meq/100 grams). 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, meq/100grams. In addition, the chemical composition of bentonite will be tested by EDAX Philip Series-40 instrument. This equipment can calculated quantitatively of bentonite element based on the emission of electron in it's orbital.

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.

Electrolysis Treatment Process

Electrolysis treatment processes were prepared firstly by making the electrolyte solutions. In this study Na_2CO_3 electrolyte solutions will be vary from 0.5% to 7.5%. DC power supply was used as power source. Both the areas of the Aluminum cathode and anode were 15 cm^2 (1 cm x 15 cm). Firstly, 5 grams bentonite were mixed by electrolyte solutions till homogenous. Then the electrode was inserted into the container by clipping the electrode and connected with DC power supply. The operating conditions for electrolysis were applied by ranging electrical potential 6V, 9V, 12V. Then, by applying different concentration of Na_2CO_3 and different electrical potential, chemical properties of bentonite was investigated by CEC test. The optimum result of CEC then tested with physical and chemical properties, and performance test for bentonite as drilling mud material and oilwell cement additives (free water) also be tested.

The expected result of the electrolysis treatment process as follows :

$$Na_2CO_3(s) \longrightarrow 2Na^+(aq) + CO_3^{2-}(aq)$$

$$2H_2O(aq) \longrightarrow 2H^+(aq) + 2OH^-(aq)$$

$$2OH^-(aq) + 2Na^+(aq) \longrightarrow 2NaOH(aq)$$

$$2H^+(aq) + CO_3^{2-}(aq) \longrightarrow H_2CO_3(aq)$$

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$$Na_2CO_3(s) + 2H_2O(aq) \longrightarrow 2NaOH(aq) + H_2CO_3(aq) \quad \text{(3-1)}$$

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 :

$$CaX \longrightarrow Ca^{++} + X^{2-} \quad \text{(3-2)}$$

$$MX \longrightarrow M^+ + X^- \quad \text{(3-3)}$$

And the final reaction from equations 3-2 and 3-3 will produce Na-bentonite, in the formula :

$$2Na^+ + X^{2-} \longrightarrow Na_2X \quad \text{(3-4)}$$

RESULT AND DISCUSSION

Chemical Composition

From the chemical composition determination showed that sodium content of untreated Sabah bentonite ranging from 0.69% to 1.52%, while standard bentonite is 3.87%, as shown in Table II. This sodium value of untreated Sabah bentonite is slightly lower when compared with standard bentonite. From this statement, it is necessary to develop Sabah bentonite performance to meet standard bentonite performance Sodium content of Sabah bentonite increased after treatment process, which were 3.2% to 4.6%. This increment of sodium means that there is an ion exchange as described above.

Cation Exchange Capacity

As shown in Table III, the CEC of untreated Sabah bentonite slightly lower when compared with standard bentoite. But after treatment process the CEC value of Sabah bentonite inscresed as follows : for M4 becomes 25 meq/100 grams at 6 volt and 9 volt for 0.5% Na_2CO_3 electrolyte solution (wt./vol), 52 meq/100 grams for SA51 at 9 volt for 0.5% Na_2CO_3 electrolyte solution (wt./vol), 66 meq/100 grams for SA54 at 9 volt for 0.5% Na_2CO_3 electrolyte solution (wt./vol), as shown in Table IV. When these untreated and treated M4, SA51, SA54 CEC values were compared with standard bentonite (82 meq/100 grams), these samples fail to reach the standard by using standard bentonite CEC. In addition, their CEC value also fail to reach montmorillonite CEC. The higher CEC value indicates higher in sodium content, thus also indicates their plastic properties. The different of plastic properties will be great of small depending on the CEC of bentonite.

MC, MA, IL

The moisture content for untreated and treated Sabah bentonite is around 10%, as shown in Table V. Moisture absorption for untreated M4 is 10.45%, after the treatment procress its moisture absorption decreased with the value 7.69%, for untreated SA51 is 14.65%, after treatment process its moisture absorption increased to 17.03%. In addition, the moisture absorption of untreated SA54 is 21.53%, after the treatment process increased to 20.22%. These moisture absorption value fail to meet standard bentonite, which is 27.61%, as shown in Table V. Moisture absorption shows the ability of bentonite to absorb a number of water. Ignition Loss for untreated and treated M4, SA51 and SA54 ranging from 7.7% to 11.2%, as shown in Table V, due to crystal bound water and CO_2 were driven off from the samples when heated at 1000 °C for an hour.

Atterberg Limit

When treated M4 is tested for Atterberg Limit, the Plasticity Index (PI) decreased into 31.72 from original value of 51.34. For treated SA51 and SA54, the situation are slightly different which are 156.92 from original value of 36.79 for SA51 and 268.05 from original value of 81.22 for SA54. These PI values for Mansuli and Adrassy bentonite fail to meet standard bentonite, which is 590.53, as shown in Table VI. It means that Mansuli and Andrassy bentonites are not the sodium montmorillonite (sodium bentonite) type since PI for the standard bentonite is sodium montmorillonite, with the ordered as followed: M4-T < SA51-T < SA54-T < Standard Bentonite.

Performance Test in Drilling Mud & Oilwell Cement

As shown in TableVII, the untreated and treated Mansuli and Andrassy bentonites could not fulfill API Spec 13A. But, the treated Mansuli and Andrassy bentonite performance as drilling mud material can be improved by at least 4% Carboxyl Methyl Cellulose High Viscosity (CMC HV) addition to meet the requirement, as shown in Table VIII. From this table, it was shown clearly that the treated SA54 is the only sample can fulfill API Spec 13A for viscometer dial reading at 600 rpm, which is 33 centipoise and filtrate volume of 9 ml. The treated bentonite performance as an additive in oilwell cementing (free water test), show that the treated SA51 ans SA54 can fulfill API Spec 10 with a volume of 1.4% and 1.2% respectively. While for treated M4 sample, it was unsuitable since it does not fulfill the requirement, since the value for M4 sample is 1.68% .

CONCLUSION

The bentonite upgrading based on electrolysis treatment can be achieved by applying electrical potential at 9 volt for SA54 bentonite. It was found that the highest CEC is 66 meq/100 grams from original value of 54 meq/100 grams. In addition, Sabah bentonite can not meet API Spec 13A of drilling mud material. Otherwise, the treated bentonite performance as drilling mud material can be improved by 4% CMC HV addition. In addition, treated bentonite can meet API Spec 10 as an additive in oilwell cementing.

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

Mineral	CEC, meq/100 grams
Kaolinite	3 – 15
Halloysite $2H_2O$	5 – 10
Halloysite $4H_2O$	10 – 40
Montmorillonite	80 – 150
Illite	10 – 40
Vermiculite	100 – 150
Chlorite	10 – 40
Sepiolite-Attapulgite	20 – 30

Table II : Chemical Composition of Untreated and Treated Mansuli (M4) and Andrassy (SA51 & SA54) Bentonite

Element		Untreated			Treated		
	Std Bent	M4-U	SA51-U	SA54-U	M4-T	SA51-T	SA54-T
NaK	3.87	1.52	0.94	0.69	3.15	4.57	4.1
MgK	3.49	3.56	2.91	2.32	2.04	2.32	2.55
AlK	14.64	18.68	18.48	19.06	9.19	18.82	20.83
SiK	51.48	53.82	51.83	57.02	67.19	44.48	48.57
P K	2.91	3.49	2.85	2	3.62	2.72	3.4
ClK	1.13	1.16	0.29	0.42	0.67	0.81	1.42
K K	0.47	6.14	0.96	2.43	3.69	0.9	2.07
CaK	2.64	1.18	2.51	3.31	0.65	2.28	2.76
Ti K	1.1	1.86	1.33	1.01	1.32	0.32	2.24
MnK	0.54	0.86	0.56	0.19	1.1	3.31	1.12
FeK	17.72	7.73	17.34	11.56	7.39	19.49	10.94
Total	99.99	100	100	100.01	100.01	100.02	100

Figure III : Cation Exchange Capacity of Untreated Mansuli and Andrassy Bentonite

Sample	CEC, meq/100 grams
Standard Bentonite	82
M4-U	23
SA51-U	41
SA54-U	54

Figure IV : Cation Exchange Capacity of Treated Mansuli and Andrassy Bentonite

Na_2CO_3 Concentration	CEC, meq/100 grams								
	M4-T			SA51-T			SA54-T		
	6 volt	9 volt	12 volt	6 volt	9 volt	12 volt	6 volt	9 volt	12 volt
0.50%	25	25	24	47	52	49	63	66	63
1.00%	24	24	24	48	48	49	64	64	63
1.50%	25	23	23	47	48	47	64	65	61
5.00%	24	23	23	44	47	50	64	65	63
7.50%	24	23	23	47	45	45	64	62	63

Table V : Moisture Content, Moisture Absorption and Ignition Loss

Sample	MC, %	MA, %	IL
Std Bent	13.43	27.61	8.76
M4-U	4.88	10.45	8.53
M4-T	4.9	7.69	7.69
SA51-U	10.62	14.65	11.11
SA51-T	8.7	17.03	11.23
SA54-U	9.49	21.53	11.31
SA54-T	10.29	20.22	10.29

Table VI : Atterberg Limit

Sample	LL	PL	PI = LL - PL
Std Bent	648.17	57.64	590.53
M4-U	81.13	29.79	51.34
M4-T	66.53	34.81	31.72
SA51-U	69	32.21	36.79
SA51-T	192.49	35.57	156.92
SA54-U	122.95	41.73	81.22
SA54-T	306.95	38.90	268.05

Table VII : Suspension Properties of Untreated and Treated Mansuli (M4-T) and Andrassy (SA51-T & SA54-T) Bentonite Used as a Drilling Mud Material.

Sample	600 rpm	300 rpm	PV, cp	YP, $lb/100\ ft^2$	GS 10", $lb/100\ ft^2$	GS 10', $lb/100\ ft^2$	Filtrate, cc
API Spec. 13A	*30, min*			*3 x PV*			*15, min*
Std Bent	32	27	5	22	31	52	14
M4-U	2.5	1.5	1	0.5	0	0	116
M4-T	1	0	1	-1	0	0	57
SA51-U	3.5	2	1.5	0.5	0	0	45
SA51-T	4	2	2	0	1	1	18
SA54-U	4.5	2.5	2	0.5	0	0	46.5
SA54-T	7	5	2	3	2	1	16

Table VIII : Suspension Properties of Treated Bentonite with CMC HV Addition Used as a Drilling Mud Material.

Sample	600 rpm, cp	300 rpm, cp	PV, cp	YP, lb/100 ft^2	GS 10”, lb/100 ft^2	GS 10’, lb/100 ft^2	Filtrate, cc
API Spec. 13A	*30, min*			*3 x PV*			*15, min*
Std Bent	32	27	0	0	31	52	14
M4, 1% CMC	5	3	5	27	0	0	22
M4, 2% CMC	8	5	2	-2	0	0	13
M4, 3% CMC	11	6	3	3	0	0	11
M4, 4% CMC	14	8.5	5	3	0	0	10
SA5-1, 1% CMC	7	4	5.5	3.5	0	1	14.5
SA5-1, 2% CMC	8	4	3	-1.5	0	1	12
SA5-1, 3% CMC	21	13	4	1	1	14	11.5
SA5-1, 4% CMC	23	15	8	9	1	10	12.5
SA5-4, 1% CMC	10	6	8	7	1	3	11
SA5-4, 2% CMC	16	10	4	-2	1	9	10.5
SA5-4, 3% CMC	24	16	6	6	3	25	10
SA5-4, 4% CMC	33	22	8	10	6	47	9

Table IX : Free Water Performance

Sample	Free Water, ml	Free Water, %
API Spec. 10	*3.5*	*1.4*
Std Bent	2.1	0.84
M4-U	2	0.8
M4-T	4.2	1.68
SA51-U	3.7	1.48
SA51-T	3.5	1.4
SA54-U	4	1.6
SA54-T	3	1.2