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# OPTIMUM WET TREATMENT PROCESS FOR UPGRADING ANDRASSY AND MANSULI BENTONITE AND THEIR APPLICATIONS IN PETROLEUM INDUSTRY

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## KEYWORDS

**Bentonite, wet treatment, chemical and physical properties, drilling mud, oilwell cement.**

## ABSTRACT

Bentonite from two areas of Sabah, Andrassy and Mansuli had been proven as non-sodium based bentonite, which is different from standard bentonite used in petroleum industry. This study complies a wet treatment process to upgrade the low quality non-sodium based bentonite to sodium based variety. Several sodium sources have been studied but only the sodium carbonate can successfully be used to upgrade these bentonite. Other parameters that included in this study are bentonite to sodium carbonate solution ratio (moisture), sodium carbonate concentration, treatment time and pH. The results obtained after wet treatment indicate improvement of cation exchange capacity varying from 22% to 36% of the original CEC values. However, the upgraded bentonite failed to fulfil the API (American Petroleum Institute) requirements for rheological properties when used as material in drilling mud and oilwell cement. Thereafter, certain polymer extender had been added to improve rheological properties of the upgraded bentonite slurry so that it can be used as a drilling mud material and oilwell cement additive. Generally, the degree of bentonite quality improvement mainly depend on the origin of bentonite itself, it's composition, especially the percentage of montmorillonite content in bentonite, chemical used in the treatment process and it's concentration, and treatment time.

## INTRODUCTION

In order to reduce the overall cost of bentonite used in local oil and gas industry, the feasibility study of Mansuli and Andrassy bentonite application had been initiated. Before these bentonite can be used, their physical and chemical properties and their performance as compared with the standard bentonite must be determined. Their performance are not as good as standard bentonite, therefore treatment method ought to be applied to convert the counter ion that placed between the unit clay surfaces. In this study, wet treatment process will be used to determine the most optimum condition in which the treatment process can be run effectively and has the ability to produce good and higher quality sodium-based bentonite as material in petroleum industry. There are four sources of samples that used in this study, three sources namely SA5-1, SA5-3 and SA5-4 from Andrassy of Tawau area and the other source namely M4 from Mansuli area of Lahad Datu in Sabah. These bentonite are believed to be non-sodium based, which are different from the commercial sodium based bentonite. Wet treatment process is developed to replace the calcium ions lies between unit clay surfaces with sodium ions. This will convert the Andrassy and Mansuli bentonite to sodium based bentonite. After treatment, the treated bentonite will be underwent a series of testing based on API (American Petroleum Institute) and OCMA (Oil Companies Materials Association) specifications as drilling muds material and oilwell cement additive. Of course, comparison will be made between the performance of treated Andrassy, Mansuli bentonite and standard bentonite.

## METHODOLOGY

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 blend 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 expressed in equation (1);

$$2Na^{+} + \text{Ca-bentonite} \longrightarrow Ca^{2+} + \text{Na-bentonite} \quad \ldots\ldots\ldots\ldots \quad (1)$$

## RESULTS AND DISCUSSIONS

### ADDITIVE SELECTION

There are commonly few of the additive that been used as sodium source in wet treatment. Sodium carbonate and sodium chloride are the most popular additives used as described by previous researchers for cation exchange purpose. The results in TABLE 1 clearly showed that there are improvement in cation exchange capacity (CEC) values of bentonite samples after the sodium carbonate is used as an additive in the wet treatment. But for the treatment using sodium chloride as an additive, negative results are obtained. After investigation, there are few factors that influence the failing of sodium chloride act as an additive in this preliminary treatment such as treatment environment and effect of anions. The sodium carbonate solution is added to the bentonite in percentage of moisture. This produces a paste-like semisolid bentonite mixture. This condition promotes cation sorption and precipitation, which can accelerate cation diffusion and exchange throughout a system.

### OPTIMIZATION OF WET TREATMENT PROCESS

As explained in previous section, the wet treatment process is carried out by using the sodium carbonate (soda ash) as main additive. There are three parameters that had been studied including sodium carbonate concentration (by weight percent of bentonite), moisture of humidity of the mixture (water to bentonite ratio) and treatment time and CEC change is used as the monitoring parameter for optimization.

#### a) Effect of Sodium Carbonate Concentration on Cation Exchange Capacity of Bentonite

The term concentration here means the amount of sodium carbonate that dissolves in the distilled water and this solution ($Na_2CO_3$ + distilled water) is used as main material to treat the bentonite samples. Generally, the CEC of bentonite increased with the increment of sodium carbonate concentration, until a maximum value. After that, CEC will start to drop from that value. For bentonite sample SA5-1, the optimum concentration of sodium carbonate for treating the SA5-1 sample is 3 % by weight of bentonite. The highest possible CEC value that can be gathered is 53 meq/100 g.

Same as SA5-1 sample, the highest possible CEC value achieved by SA5-3 sample is also 53 meq/100 g, when the $Na_2CO_3$ concentration is 2 %. However, SA5-4 sample is considered the best among the local bentonite and has an original CEC value nearest to the standard bentonite, 54 meq/100 g. The CEC value for SA5-4 sample after wet treatment is 66 meq/100 g (see FIGURE 1). It is indicated that the optimum concentration of $Na_2CO_3$ is 4 % by weight of bentonite, with 200 % of moisture. The treatment of this sample successfully produced a good result in CEC value, a promising value as compared to other samples. The last sample is M4 bentonite, which is sampling from Mansuli area. It is meaningless to show the results of this sample because there is no any increment of CEC value for this sample. The reason of why M4 sample cannot be upgraded will be discussed later in this paper.

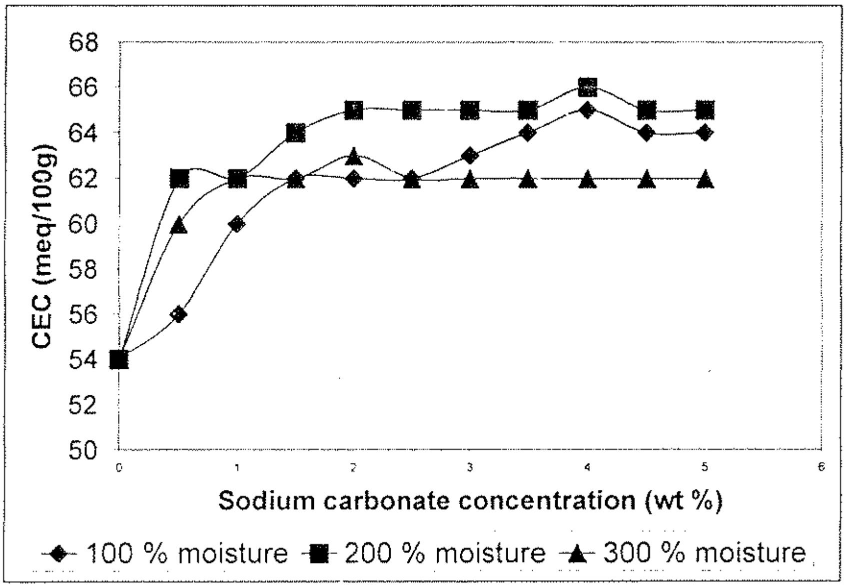

**FIGURE 1: Effect of sodium carbonate concentration on CEC values of SA5-4 sample (after 96 hours).**

**b) Effect of Moisture on Cation Exchange Capacity of Bentonite**

As shown in FIGURE 2, the moisture of the wet treatment plays an important part for cation exchange reaction on the unit layers surface of bentonite. The range of moisture that used in this study was set from 100 % to 300 % by weight of the bentonite sample. The trend lines for FIGURE 2 generally indicated that the moisture is directly proportional to the cation exchange rate of bentonite sample. However, after reaching a maximum value of CEC, the trend line will start to drop except for SA5-3 sample. This can be concluded that the wet treatment process should not be run very high moisture condition unless the presence of material that can avoid the swelling of bentonite.

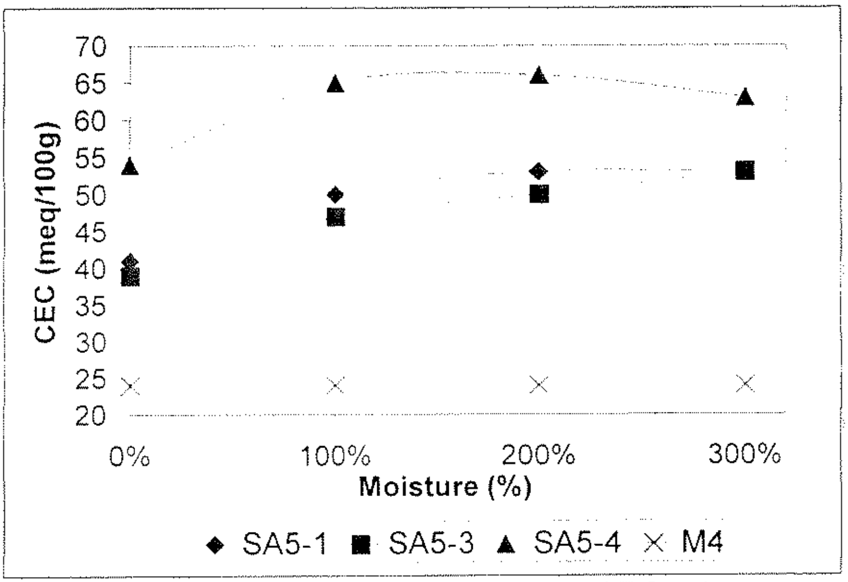

**FIGURE 2: Effect of moisture on the CEC values.**

As we know, bentonite is clay that has very high swelling ability compared to other clay minerals. If the bentonite contact with a large amount of water before the cation exchange reaction, the water will occupied between the bentonite unit layers and causing it to hydrate or swell. This "envelope" of water will surely blocks the paths for sodium ions that are ready to replace the calcium ion and thus decrease the entire cation exchange reaction of the treatment process

**c) Effect of Treatment Time on Cation Exchange Capacity of Bentonite**
Treatment time always associated with the cation exchange rate of montmorillonite mineral, which is the main component in bentonite. From the results obtained, it can be concluded that the cation exchange rate of wet treatment process for SA5-1, SA5-3 and SA5-4 bentonite samples reached a maximum degree after 48 hours (2 days). This means the cation exchange reaction for these bentonite samples (SA5-1, SA5-3 and SA5-4) had stopped or finished.

## BENTONITE PHYSICAL PROPERTIES

TABLE 2 shows the Atterberg limits of Andrassy and Mansuli bentonite as compared to the standard bentonite before and after wet treatment process. The method adopted for liquid limit is three points graphical liquid limit determination method). With refer to the plastic limit versus plasticity index graph, the treated SA5-1 and SA5-3 samples had been fallen into area between the calcium montmorillonite and sodium montmorillonite areas. SA5-4 sample, the other sample from Andrassy can be categorized as sodium montmorillonite after wet treatment because of its better liquid limit and plasticity index values. In addition, there is only a little change of position for M4 sample in the graph, in the area of plastic kaolin.
Moisture content, moisture adsorption and ignition loss are important to determine the physical properties of clay roughly, especially for bentonite. Generally, the API and OCMA requirement for bentonite are 10 % and 13 % weight percent maximum, respectively. From TABLE 3, it is clearly shows that the Andrassy and Mansuli bentonite fulfill these requirements except for the untreated SA5-3 sample, which fail to meets the API requirement, with a MA value up to 12 %. From the results, it is clearly showed that there is only a slightly increased in MA value for SA4-3, SA5-4 and M4. But for SA5-1 sample, the MA has been increased from 11.91 % to 17.25 %. In addition, there is no much difference for the ignition loss of the bentonite samples before and after treatment.

## BENTONITE CHEMICAL PROPERTIES

Specific surface of clay is expressed in $m^2/g$. The specific surface results of bentonite samples as compared to standard bentonite is as shown in TABLE 4. The results indicated that all the Andrassy and Mansuli bentonite showed improvement in specific surface. As expected, the treated Andrassy bentonite samples (SA5-1, SA5-3 and SA5-4) give a more satisfy results if compare to the M4 sample. More than 100 $m^2/g$ specific surface improvements had been indicated for Andrassy bentonite samples.
Chemical composition of bentonite can be analyzed using the Scanning Electron Microscope (SEM) with EDAX. The chemical composition of bentonite of SA5-1, SA5-3, SA5-4 and M4 have been tested and compared to the chemical composition of standard bentonite as shown in TABLE 5. It is indicated that the Na compound after wet treatment had been increased for the bentonite samples of SA5-1, SA5-3, SA5-4 and M4. SA5-4 sample has the highest content of Na among the bentonite samples followed by SA5-3, M4 and SA5-1 sample. However, it was not all the Na detected by EDAX is the truly interlayer cation between the bentonite particle layers. Only part of the Na is successfully replacing the calcium in the interlayer and the remaining Na detected is considering as residue cation.

## BENTONITE PERFORMANCE AS DRILLING MUD MATERIAL

The API and OCMA specifications as well as the suspension properties of untreated Andrassy and Mansuli bentonite are showed in TABLE 6. The results indicated that the suspension properties of all the untreated Andrassy and Mansuli bentonite failed to meet the requirements except for the moisture content. Although the yield point over plastic viscosity ratio for untreated bentonite fulfilled the requirements, but the viscosity at dial reading 600 rpm for untreated local bentonite is very low.

After being treated with sodium carbonate, the Andrassy and Mansuli bentonites had been tested for their rheological properties with refer to the specification that have mentioned. Since the moisture content of the bentonite samples were tested and discussed in previous section, this discussion of this parameter will not be repeated. In addition, because of the treated bentonite samples did not satisfying the standard requirements, two types of polymer extender had been added to the bentonite suspension. These polymers are partially hydrolyzed poly-acrylamide (PHPA) and high viscosity carboxymethyl cellulose (CMC). The results of the 600 rpm dial readings after wet treatment are as shown in FIGURE 3. From the trend lines for both figures, the 600 rpm dial reading is directly proportional to the increment of the polymer extender concentration. The bentonite suspensions with PHPA show higher value of the reading as compared to the one with CMC. However, all the bentonite samples failed to meet the API and OCMA requirements with a maximum allowable polymer extender of 2 % by weight of bentonite. From the FIGURE 3, it is indicated only the SA5-4 sample (with 3 % of polymer extender) successfully reached the minimum requirement of 600 rpm dial reading.

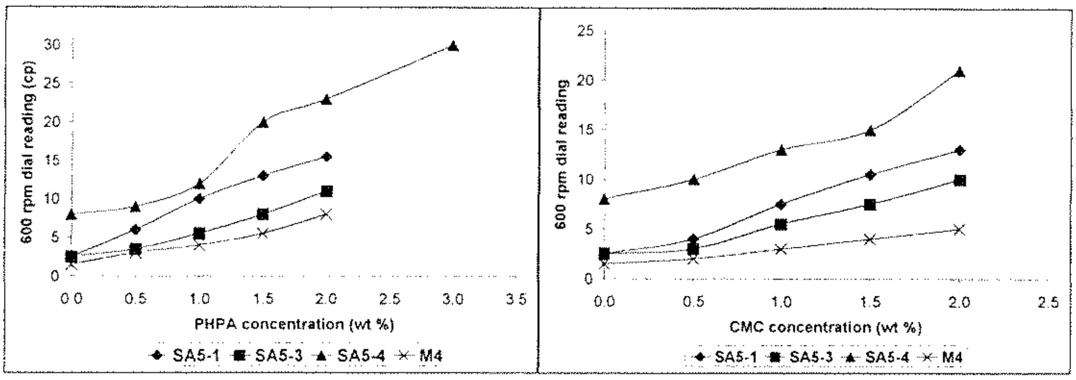

**FIGURE 3: 600 rpm dial reading of bentonite suspensions with the addition of PHPA (left) and CMC (right).**

Another important parameter that required by the API and OCMA specifications is the yield point (YP) over plastic viscosity (PV) ratio. Same as the samples before wet treatment, all the samples with CMC and PHPA added successfully fulfill the standard specifications.

From FIGURE 4, it is observed that all the treated bentonite samples (without extender) are failed to meet the standard requirements. After being added with polymer, there are trends there the fluid loss decreased with the increment of polymer extender. Among these samples, SA5-4 can be considered have the most satisfied fluid loss control with just 0.5 % of PHPA was added.

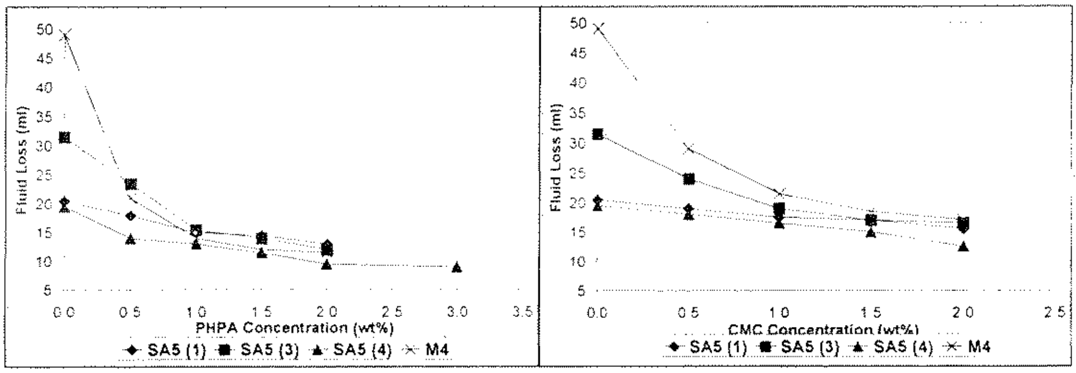

**FIGURE 4: 30 minutes fluid loss of bentonite suspensions with the addition of PHPA (left) and CMC (right).**

## BENTONITE PERFORMANCE AS OILWELL CEMENT MATERIAL

In general, the untreated bentonite samples have less capability to build up filter cake of low permeability as well as having low swelling capacity. However, after wet treatment, there is improvement in the dispersed filtrate volume for the Andrassy and Mansuli bentonite.

It is observed that the untreated Andrassy and Mansuli bentonite cannot meet the minimum requirement of free water content. After the treatment process, only SA5-4 sample can successfully provide a minimum value of the free water content with 3.5 ml or 1.4 % by volume of the entire cement system. SA5-1 and SA5-3 samples also show improvement but yet to reach the desired minimum requirement. Due to its low montmorillonite mineral content, the M4 sample shows no improvement in the free water control capability.

## CONCLUSION

After being treated with optimum wet treatment process, the Andrassy bentonite samples show improvement in various aspects such as chemical composition, physical and chemical properties. Conversely, the Mansuli sample (M4) failed to do so because of its mineral limitation in montmorillonite mineral. In general, the Andrassy and Mansuli bentonite do not satisfy the requirements when used as drilling mud and oilwell cement material. But the addition of some polymer successfully improved the entire rheological properties of the Andrassy bentonite samples when used as drilling mud material. In oilwell cement, Andrassy and Mansuli bentonite failed to exhibit better performance after wet treatment. However, the facts showed that the cation exchange for this wet treatment was successful since there are many evidences that indicated the non- sodium based bentonite had been successfully upgraded to the sodium variety.

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TABLE 1: Bentonite CEC value after wet treatment by using different types of additive.

| CEC value (meq/100g) | Sodium carbonate | | | | Sodium chloride | | | |
|---|---|---|---|---|---|---|---|---|
| | SA5-1 | SA5-3 | SA5-4 | M4 | SA5-1 | SA5-3 | SA5-4 | M4 |
| before | 41 | 39 | 54 | 24 | 41 | 39 | 54 | 24 |
| after | 47 | 45 | 61 | 24 | 36 | 34 | 48 | 18 |

TABLE 2: Comparison of the Atterberg limit of bentonite samples before and after wet treatment as compared to standard bentonite.

| Sample | Liquid Limit (%) | | Plastic Limit (%) | | Plasticity Index (%) | |
|---|---|---|---|---|---|---|
| | before treatment | after treatment | before treatment | after treatment | before treatment | after treatment |
| **Standard Bentonite** | 583.12 | - | 57.64 | - | 524.48 | - |
| **SA5-1** | 68.32 | 219.50 | 32.21 | 50.21 | 36.11 | 169.30 |
| **SA5-3** | 63.35 | 167.40 | 32.12 | 42.59 | 32.53 | 124.80 |
| **SA5-4** | 122.84 | 248.50 | 42.36 | 45.83 | 80.48 | 202.70 |
| **M4** | 79.69 | 65.80 | 29.79 | 30.66 | 49.90 | 35.20 |

TABLE 3: MC, MA and IL values of Andrassy and Mansuli bentonite as compared to standard bentonite.

| Sample | Moisture Content (%) | | Moisture Adsorption (%) | | Ignition Loss (%) | |
|---|---|---|---|---|---|---|
| | before treatment | after treatment | before treatment | after treatment | before treatment | after treatment |
| **Standard Bentonite** | 4.88 | - | 30.31 | - | 8.53 | - |
| **SA5-1** | 9.39 | 5.63 | 11.91 | 17.25 | 10.32 | 10.03 |
| **SA5-3** | 11.94 | 5.26 | 17.54 | 17.89 | 11.27 | 11.11 |
| **SA5-4** | 9.49 | 7.91 | 21.53 | 21.58 | 11.31 | 11.03 |
| **M4** | 7.39 | 1.69 | 9.51 | 10.85 | 9.31 | 7.51 |

TABLE 4: Specific surface of bentonite samples before and after wet treatment.

| Sample | Specific Surface ($m^2$/g) | |
|---|---|---|
| | before treatment | after treatment |
| Std-Ben | 819.62 | - |
| SA5-1 | 324.18 | 526.02 |
| SA5-3 | 293.59 | 452.62 |
| SA5-4 | 434.28 | 636.12 |
| M4 | 151.69 | 204.29 |

**TABLE 5: Chemical composition of bentonite of SA5-1, SA5-3, SA5-4 and M4 as compared to standard bentonite.**

| Chemical compound | Std-Ben | SA5-1 | | SA5-3 | | SA5-4 | | M4 | |
|---|---|---|---|---|---|---|---|---|---|
| | | before | after | before | after | before | after | before | after |
| Fe | 13.98 | 7.00 | 6.03 | 9.87 | 8.11 | 3.66 | 3.44 | 13.39 | 12.17 |
| Na | 4.13 | 0.73 | 2.39 | 1.43 | 5.15 | 0.39 | 6.28 | 1.62 | 5.10 |
| Mg | 5.15 | 1.51 | 3.12 | 2.42 | 2.48 | 2.00 | 2.63 | 2.60 | 3.74 |
| Al | 15.84 | 29.64 | 24.41 | 25.12 | 23.11 | 24.18 | 21.41 | 16.36 | 18.83 |
| Si | 57.58 | 57.91 | 60.86 | 57.03 | 56.88 | 60.72 | 61.33 | 60.25 | 53.18 |
| K | 0.51 | 0.82 | 0.96 | 1.19 | 1.66 | 2.84 | 1.53 | 4.02 | 5.61 |
| Ca | 1.88 | 1.71 | 1.51 | 2.14 | 1.82 | 4.95 | 3.05 | 0.70 | 0.36 |
| Mn | 0.94 | 0.68 | 0.72 | 0.81 | 0.79 | 1.26 | 0.33 | 1.05 | 1.01 |
| Total | 100.01 | 100.00 | 100.00 | 100.01 | 100.00 | 100.00 | 100.00 | 99.99 | 100.00 |

**TABLE 6: The suspension properties of untreated Andrassy and Mansuli bentonite as compared to API and OCMA requirements.**

| Requirement | API 13A spec. | OCMA spec. | SA5-1 | SA5-3 | SA5-4 | M4 |
|---|---|---|---|---|---|---|
| Viscometer Dial Reading at 600 rpm | 30, min | 30, min | 5 | 5 | 5 | 4.5 |
| Yield Point/Plastic Viscosity Ratio | 3, max | 6, max | 0.5 | 0.5 | 0.5 | 0.5 |
| Filtrate Volume | 15.0 cm$^3$, max | 16.0 cm$^3$, max | 64cm$^3$ | 79cm$^3$ | 52cm$^3$ | 114cm$^3$ |
| Moisture | 10.0 wt%, max | 13.0 wt%, max | 9.65 wt% | 8.73 wt% | 5.99 wt% | 4.88 wt% |

**TABLE 7: The properties of untreated and treated Andrassy and Mansuli bentonite as oilwell cement material as compared to API specification requirements.**

| Requirement | API Spec. | SA5-1 | | SA5-3 | | SA5-4 | | M4 | |
|---|---|---|---|---|---|---|---|---|---|
| | | before | after | before | after | before | after | before | after |
| YP/PV ratio | 1.5, max. | 0.5 | 0.50 | 0.50 | 0.50 | 0.50 | 0.67 | 0.50 | 0.50 |
| Dispersed Plastic Viscosity | 10 cp, min. | 2 | 1 | 2 | 1 | 2 | 3 | 2 | 1 |
| Dispersed Filtrate Volume | 12.5 ml.max. | 64.0 ml | 20.5 ml | 79.0 ml | 31.5 ml | 52.0 ml | 19.5 ml | 114.0 ml | 49.0 ml |
| Free Water | 3.5 ml. max. | 4.50 ml | 3.75 ml | 5.00 ml | 4.00 ml | 3.75 ml | 3.50 ml | 4.25 ml | 4.25 ml |