



Comparative Analysis of the Effect of Cation Exchange Capacity (CEC) on Raw and Treated Nigerian Bentonitic Clay Samples

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Abstract The Cation Exchange Capacity (CEC) of the Nigerian bentonitic clay samples obtained from the North Eastern Nigeria, namely: Garin Hamza, Pindiga, Tongo, BulabulinMaiduwa and SabonGarinNgalda were investigated using Methylene Blue method. The raw samples were beneficiated using wet beneficiation method to reduce the excess silica content and further activated with Na₂CO₃ to become Sodium based bentonite used for drilling fluid formulation. The CEC values for raw Nigerian Bentonitic clay samples ranges from 12 to 44 meq/100 g which have low values compared to standard (57.9 meq/100g). The CEC values significantly increased compared to the raw samples after silica (Quartz) reduction between 31.3 to 46.0 meq/100g. The CEC values remain relatively the same even after activation with Na₂CO₃, except Tongo bentonite with CEC value of 38.9 meq/100g for raw bentonite that reduced to 34.9 after silica reduction but on activation with Na₂CO₃ the value rose to 39.7 meq/100g. It was generally observed that the CEC values of all the formulated drilling fluid for the treated samples slightly reduced due to the effect of the viscosifier (Poly anionic cellulose) used during formulation.

Keywords Cation Exchange Capacity, Bentonite, Activation, Silica and Poly Anionic Cellulose.

Introduction

The importance of bentonite as a mud in drilling operations in water, oil and gas well construction cannot be overemphasized. The cost of drilling is reduced by about 15% when drilling mud is used and this is not small given the overall cost of drilling an oil or gas well [1].

The term "bentonite" is defined geologically as a rock formed of highly colloidal and plastic clays composed mainly of montmorillonite, a clay mineral of the smectite group, and is produced by in situ devitrification of volcanic ash [2]. The transformation of ash to bentonite apparently takes place only in water (certainly seawater, probably alkaline lakes, and possibly other fresh water) during or after deposition [3, 4]. Bentonite was named after Fort Benton (Wyoming, USA), the locality where it was first found.

In oil field parlance, bentonite is classified as sodium bentonite or calcium bentonite, depending on the dominant exchangeable cation. Correspondingly, in terms of performance, bentonite is classed as "high yield" or "low yield" and in terms of geographic origin as "Western" or "Southern". Bentonite supplied from the Wyoming, South Dakota and Montana deposits are considered high yield because of their superior mud-making and filtrate control qualities. This does not imply that these terms refer to distinct compositions. Although western bentonite is recognized as the highest quality clay for use in drilling mud, the colloidal properties vary, even in the same deposit. Mappable bentonite beds vary in thickness from a minimum of two feet. The maximum stripping depth is about sixty feet. After stripping, a common practice is to expose the clay to air for several



months, during which time the bed may be plowed or ripped. This practice promotes drying and improves the quality of the clay[5].

By extension, the term bentonite is applied commercially to any plastic, colloidal, and swelling clay regardless of its geological origin. Such clays are ordinarily composed largely of minerals of the montmorillonite group. The term “montmorillonite” is also ambiguous and is used both for a group of related clay minerals and for a specific member of that group [6].

The chemical composition of bentonite affects its usage [4, 7, and 8]. High swelling bentonite, in which sodium is usually the dominant exchangeable ion, is preferred for drilling muds, pelletizing iron ore, sealing and waterproofing, whereas low-swelling calcium bentonite is preferred for filtering, clarifying, absorbing and for serving as a filler, stabilizer, extender, carrier, bonding agent, or catalyst.

Bentonite feels greasy and soap-like to the touch [6]. Freshly exposed bentonite is white to pale green or blue and, with exposure, darkens in time to yellow, red, or brown [2]. The special properties of bentonite are an ability to form thixotropic gels with water, an ability to absorb large quantities of water with an accompanying increase in volume of as much as 12–15 times its dry bulk, and a high cation exchange capacity.

Substitutions of silicon by cations produce an excess of negative charges in the lattice, which is balanced by cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) in the interlayer space. These cations are exchangeable due to their loose binding and, together with broken bonds (approximately 20% of exchange capacity), give montmorillonite a rather high (about 100 meq/100 g) cation exchange capacity, which is little affected by particle size. This cation exchange capacity allows the mineral to bind not only inorganic cations such as caesium but also organic cations such as the herbicides diquat, paraquat[9], and striazines[10], and even bio-organic particles such as rheoviruses[11] and proteins [12], which appear to act as cations.

Montmorillonites also tend to have a large specific surface. Specific surface refers to the amount of surface area per material unit mass. In a dispersed system, this can be defined as the surface area per gram or surface area per unit volume of the system [13]. As montmorillonites have the largest specific surface among the major clay minerals, montmorillonitic soil layers can easily be penetrated by exchangeable ions and water. This causes the layers to separate and the soil experiences relatively large volume changes [14].

The presence and type of exchangeable cations will have an effect upon the hydration, or swelling ability of clay. Strongly swelling clays, such as montmorillonite, will adsorb a water layer to the surface of the clay due to the presence of electrical charges on the surfaces and edges of the clays [15]. This water layer will vary in thickness depending upon the type of cation associated. Sodium montmorillonite will form a thicker layer which will tend to move the clay platelets farther apart and make them more susceptible to dissociation as shown in Figure1 On the other hand, calcium montmorillonite, because it is less hydratable, will provide less viscosity than sodium montmorillonite in equal quantities [16].

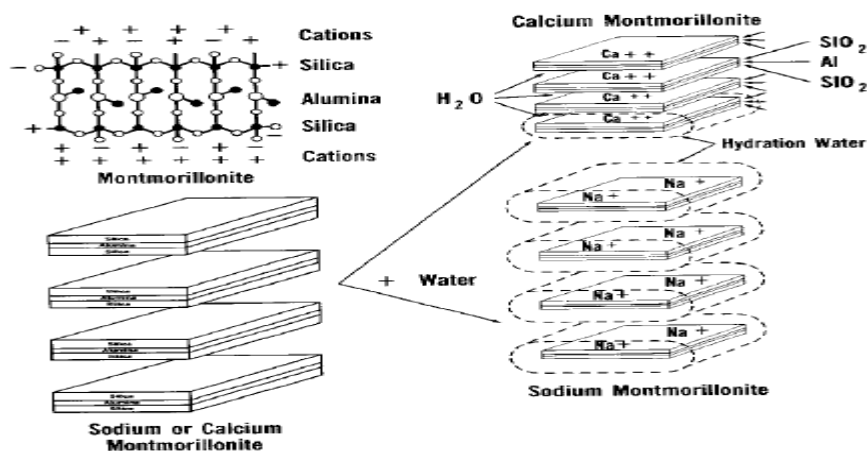


Figure 1: Hydration of Sodium and Calcium Montmorillonite[17].



Variation in exchangeable cations affects the maximum amount of water uptake and swelling. These are greatest with sodium and least with potassium and magnesium. Interstitial water held in the clay mineral lattice is an additional major factor controlling the plastic, bonding, compaction, suspension, and other properties of montmorillonite group clay minerals.

Bentonite clays also exist in the North-east quadrant of Nigeria (Borno, Yobe, Taraba and Adamawa) where a probable reserve of more than 700 million tones has been indicated [18].

The research work is aimed at estimating the concentration of exchangeable cation in both the raw and treated Nigerian Bentonitic clay samples with the objective of determining their suitability and applicability for oil and gas drilling application as compared with API standard.

Materials and Methods

Methodology for Silica Removal

The raw Bentonitic clay samples were collected from five different locations (Table 1) of the marine environment of upper Benue trough, north eastern Nigeria and were brought to the Department of Material Science laboratory, Centre for Energy Research and Training (CERT), Zaria, for further analysis.

Table 1: Collected samples and the co-ordinates of collection.

S/No.	LOCATION NAME	STATE	LOCATION ID	LATITUDE	LONGITUDE
1	Garin Hamza/Futuk	Bauchi	GHF-BA	09° 50' 43.2"N	10° 54' 10.3"E
2	Pindiga	Gombe	PND-GM	09° 58' 41.0"N	10° 57' 05.2"E
3	Tongo	Gombe	TNG-GM	10° 40' 34.6"N	11° 21' 39.0"E
4	BulabulinMaiduwa	Yobe	BBL-YB	11° 21' 50.3"N	11° 17' 13.1"E
5	SabongarinNgalda	Yobe	SGN-YB	11° 10' 15.3"N	11° 21' 14.7"E

The raw Bentonitic clay samples were wet-beneficiated in order to purify them from physically and chemically combined impurities such as metallic oxide, grits and to reduce the excess silica as explained by [19].

Activation of Beneficiated Clay with Sodium Carbonate.

The pre-treated (Quartz removed) samples were activated with Na_2CO_3 in order to convert the calcium based bentonite to Sodium based bentonite by cation exchange. The wet beneficiation method was used for this research because it was observed to be the best compared to the dry method [20]. The sodium activation was carried out at various concentrations ranges from 3 to 15 wt % added to the bentonite powder suspension in water at the interval of 3%. The suspension was thoroughly mixed for 15 minutes allowed to age for 24 hours for the ion exchange to take place. The activated samples were then dried to remove the moisture content (Plate I), ground to powder with the aid of ball mill machine and then sieved again to 63 μm . This procedure was carried out on all the samples which were packaged for characterization and drilling fluid formulation.

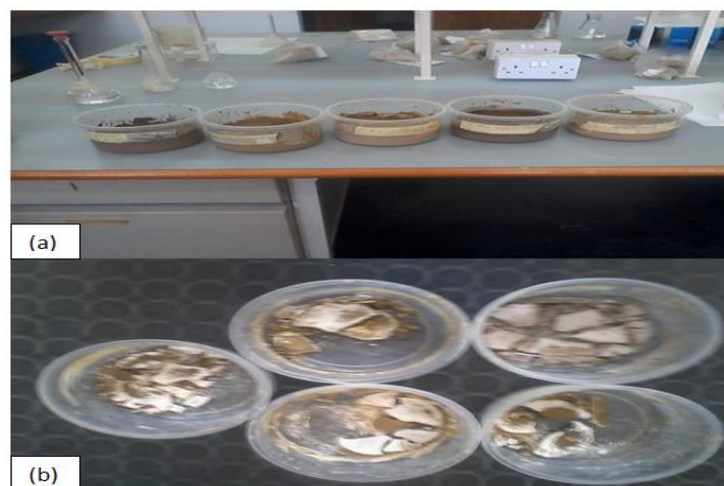


Plate I: Photograph of (a) wet bentonite undergoing CEC reaction and (b) dried Sodium (Na) activated bentonite samples.



Results and Discussion

The calculated Cation Exchange Capacity of the various bentonites samples expressed as methylene blue capacity given by equation 1, are presented in Table 1. The CEC is the total amount of cations absorbed expressed in milli equivalent per 100g of dry clay. The required values range is 70-100 meq/100g as reported by [23], but the laboratory tested Wyoming Bentonite has 57.9 meq/100g CEC value. The investigated CEC values from Table 1 ranges from 12 to 44 meq/100 g for raw Bentonitic clay, which do not fall within the normal range and implies that the local clays have low CEC. These low values could result in drilling fluids with low rheological properties especially when sodium is not in the exchange position [20 and 22] Presence of excess silica (Quartz) can also reduce the cation exchange capacity of bentonite. It was observed that when the silica content of the sample was reduced, the CEC values significantly increased compared to the raw samples. Raw Garin Hamza, Pindiga, Bulabulinmaiduwa and SabongarinNgalda were having CEC values of 14.5, 44.1, 20, and 33.3 meq/100g which increased to 36, 46, 31.3 and 34.7 meq/100g respectively. These values remain relatively the same even after activation with Na_2CO_3 , except Tongo bentonite with CEC value of 38.9 for raw bentonite that reduced to 34.9 after silica reduction but on activation with Na_2CO_3 the value rose to 39.7 meq/100g. This is probably is because an appreciable amount of Na which is soluble in water was leached out during pretreatment or silica removal and when it was regained after sodium activation with Na_2CO_3 , thus affecting the CEC values. It was generally observed that the CEC values of all the formulated drilling fluid slightly reduced, probably due to the effect of the additive (PAC) used during formulation.

Table 2: Cation Exchange Capacity of various Bentonite Samples

S/No.	Bentonite Sample Name	Raw CEC (meq/100g)	After SiO_2 (Quartz) Reduction CEC (meq/100g)	Na Activated CEC (meq/100g)	Treated CEC (meq/100g)
1	API Grade (Standard)	57.9	-	-	-
2	Garin Hamza Futuk	14.5	36.0	36.7	32.2
3	Pindiga	44.1	46.0	46.0	38.3
4	Tongo	38.9	34.9	39.7	33.9
5	BulabulinMaiduwa	20.0	31.3	31.1	29.1
6	SabongarnNgalda	33.2	34.7	34.7	38.4

Conclusion

The CEC values for raw Nigerian Bentonitic clay samples ranges from 12 to 44 meq/100 g which has low values compared to standard (57.9 meq/100g). The CEC values significantly increased compared to the raw samples after silica (Quartz) reduction to 31.3 – 46 meq/100g. The CEC values remain relatively the same even after activation with Na_2CO_3 , except Tongo bentonite with CEC value of 38.9 for raw bentonite that reduced to 34.9 after silica reduction but on activation with Na_2CO_3 the value rose to 39.7, this is probably an appreciable amount of Na which is soluble in water was leached out during pretreatment or silica removal and when it was regained after sodium activation the CEC value significantly increased to 39.7 meq/100g. It was generally observed that the CEC values of all the formulated drilling fluid slightly reduced due to the effect of the viscosifiers (PAC) used during formulation.

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