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DETERMINATION OF MORPHOLOGICAL FEATURES AND MOLECULAR INTERACTIONS OF NIGERIAN BENTONITIC CLAYS USING SCANNING ELECTRON MICROSCOPE (SEM)

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ABSTRACT

This research focused on identifying the morphological features and molecular interactions of the Nigerian Bentonitic clays using Scanning Electron Microscope (SEM) characterisation technique. The SEM microstructure images indicated that the bentonite samples are generally moderately dispersive to dispersive with some large flocs which were apparently separate and dispersed from one another rather than located on the totality of the image. This property is more pronounced on the sodium (Na) activated and the treated samples than in the raw samples, which could be due to quartz removal and Na activation on the raw Bentonitic samples. Dispersive sample surfaces consist of loose flakes with no definitive mass structures observed on the treated samples due to added poly anionic cellulose (PAC) to the samples

Key words: SEM, microstructure, images, bentonite, flocs and PAC

INTRODUCTION

Bentonite is 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. In addition to montmorillonite, bentonite may contain Feldspar, Cristobalite, and Crystalline Quartz. Bentonite feels greasy and soap-like to the touch (Bates & Jackson, 1987). Freshly exposed bentonite is white to pale green or blue and, with exposure, darkens in time to yellow, red, or brown (Parker, 1988).

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 (Grim, 1968; Patterson & Murray, 1983). Bentonite was named after Fort Benton (Wyoming, USA), the locality where it was first found. 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 (Carlos and George 2004).

The availability of bentonite in Nigeria and the wide range of industrial application enhances the attractiveness of the bentonite processing ventures. The present level of consumption in Nigeria is about 200,000 metric tons (for oil well drilling only); much of this is sourced from the foreign market (RMRDC, 2010).

Bentonite clays 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. Similarly, over 90 million tones have been reportedly found in Afuze, Ekpoma-Igunebon road, Ovibiokhuan and Okpebho areas of Edo State. Some occurrences have also been reported in Abia, Ebonyi and Anambra States. (RMRDC, 2010). Bentonite occurrence has also been reported in Benue State, (Abdullahi, 1996) in Azara; Nasarawa State and Akiri Hill in Plateau state (Onaogu, 1996).

Scanning electron microscopy is best suitable for observation of bentonite structure. The resolution is not good enough to allow observation of single clay mineral grains. Coarse-grained accessory minerals can be identified by observing their morphology and getting information about their chemical composition with help of energy dispersive X-ray spectroscopy (EDS). It is also possible to get semi quantitative chemical data on bentonites using SEM-EDS. It is necessary to analyse a great number of aggregates to get statistically reliable data (Lisa, 2004).

Montmorillonite can be identified by its microstructure. It tends to occur in thin equidimensional flakes that have a film-like appearance. The particles can have thicknesses ranging from 1-nm to about 1/100 of the particle width. The long particle axis is usually less than 1 to 2- μ m. In addition to flakes, some platy or needle particles may be seen. This occurs when there is large isomorphous substitution with the aluminium being exchanged for magnesium or iron.

These ions are larger than the aluminium ions and are reflected as such in the microstructure (Mitchell and Soga, 2005).

Montmorillonite clay minerals occur as minute particles, which, under electron microscopy, appear as aggregates of irregular or hexagonal flakes or, less commonly, of thin laths (Grim, 1968). Differences in substitution affect and in some cases control morphology.

This research focused on characterising the raw and beneficiated Bentonitic clays using Scanning Electron

Microscope (SEM) with the aim of determining morphological feature of the sampled Bentonitic clays.

METHODS AND MATERIALS

Methodology for Silica Removal

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

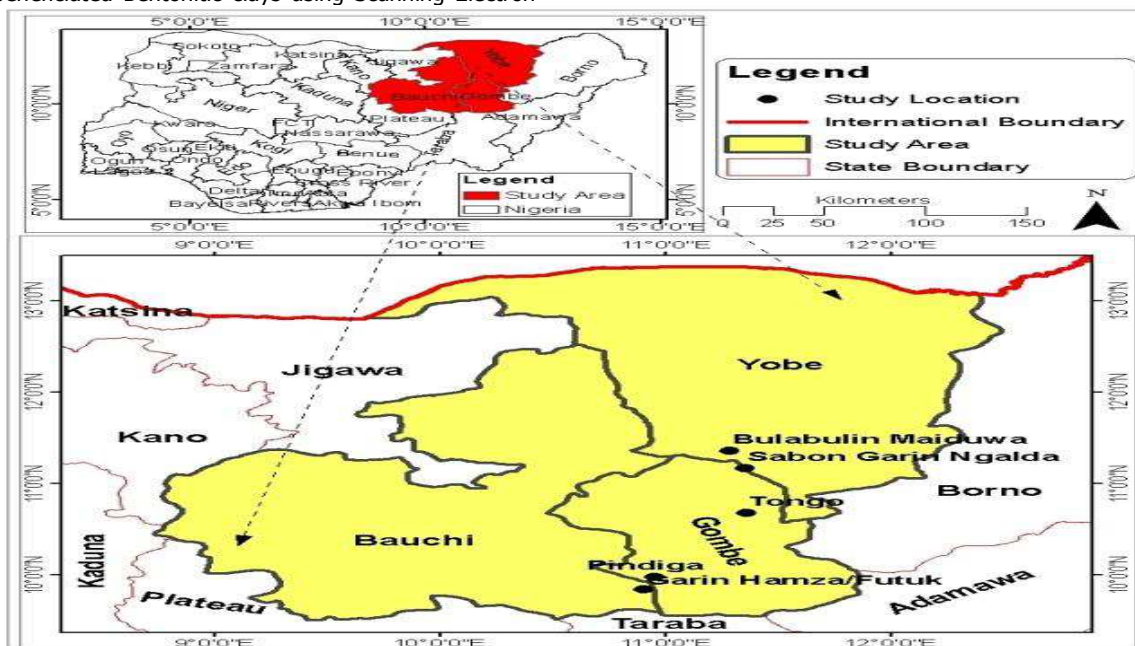


Figure 1: Map of study area showing sample locations

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. The raw clays were dried at room temperature and crushed to less than 125 μm particle size using ball mill machines. Then, the crushed samples were dissolved in water (clay-water ratio 2:5) by stirring until no lumps were present, the mixture was allowed to stay for 24 hours after which clay slurry settled into three distinct layers, the bottom coarse particles, the middle fine clay particles and the top supernatant water layer. The middle layer (clay portion) was collected for further activity after decanting the supernatant water, while the bottom coarse particles considered to be excess quartz were discarded (Bilal *et al.*, 2015). Quartz (free silica) is one of the minerals that are commonly found in the earth's continental crust. This mineral has a hexagonal crystal structure made of trigonalcrystallized silica (silicon dioxide, SiO_2), with 7 Mohshardness scale and density of 2.65 g / cm^3 , (Muhammad, 2013).

The fine clay slurry was sieved using Tyler sieve of mesh size 230 (63 μm aperture opening) so as to further separate the fine grits present in the fraction.

The resulting clay slurry was allowed to settle and the supernatant water layer was removed by leaving it for 48 hours in clay pot. Finally, the solid clay cake was dried in an oven at 60°C for 48 hours to completely dry the samples ready for Na activation (Bilal *et al.*, 2015)

Activation of Beneficiated Clay with Sodium Carbonate.

The beneficiated (Quartz reduced) 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 (Shuwa, 2010). 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), which was ground to powder with the aid of ball mill machine and then sieved again to 63 μm .



Plate I(a): Photograph of wet Bentonite undergoing CEC



Plate I(b): Photograph of dried Sodium (Na) activated Bentonite Samples.

The viscosifier (PAC) was added at predetermined maximum concentrations (0.6g in 24.5g of treated Pindiga Bentonite and 0.8g in 24.5g for each of the remaining treated samples). This procedure was carried out on all the samples which were packaged for characterization and drilling fluid formulation as explained by Bilal *et al.*, (2006).

Scanning Electron Microscope (SEM) Analysis

SEM imaging was carried out in the Materials Analysis and Research Laboratory of the Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria. A Phenom ProX desktop scanning electron microscope (SEM) was used to analyse the morphological features of the raw, Na activated, and treated bentonites of the five different samples from different locations.

Scanning Electron Microscopy (SEM) is an electron that describes the sample by scanning a beam of

electrons in raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample surface topography, composition and properties. Scanning Electron Microscopy (SEM) aims to look at the structure and shape of the surface of bentonite (Muhammad *et al.*, 2013).

RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM) Results

The SEM results for the Bentonite samples at 1000x magnification were used for all the samples to clearly identify all the morphological clay properties and larger interactions of the samples in SEM at higher resolution.

The API grade (standard) Bentonitic clay at 1000x magnification was observed to have irregular shaped and dispersed clay minerals that could be predominantly alumina (Figure 2).

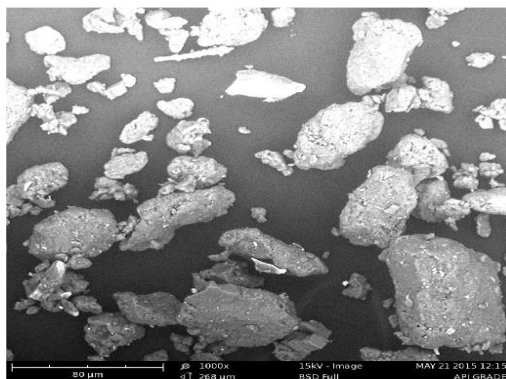


Figure 2: SEM image of API grade (Standard) Bentonite

Comparative Study of Raw, Sodium (Na) Activated and Treated Bentonite Samples

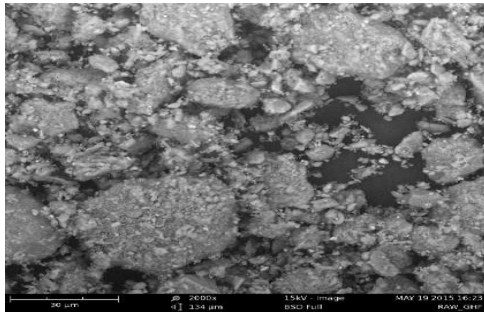
The SEM images for the raw, Na activated and treated samples presented in Figure 3 to 7 are for the purpose of comparisons and were compared at a magnification of 1000x.

The samples are discussed in the order of increased dispersion as nondispersive, slightly to moderately dispersive, and dispersive for raw, beneficiated/Na activated and treated samples respectively, depending on the nature of the morphological features and molecular interactions identified in the SEM images.

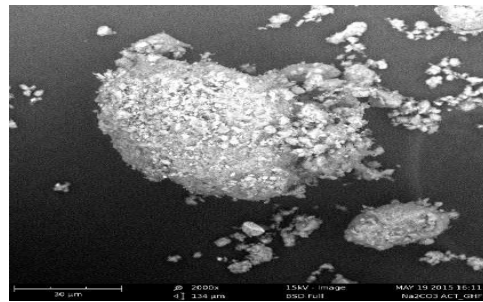
It has been observed by Sides and Barden, (1971) that in a nondispersed clay SEM image, there should be no set particle orientation and a multitude of edges, planes, and cavities in every direction. All the SEM images for the raw samples seem to display these characteristics. The voids or cavities are clearly observed easily in all of the images and moreover, the particles are well aggregated as flocs which were observed in raw Garin Hamza, Pindiga, Tongo and Sabongarin Ngalda Bentonites with the exception of raw Tongo and Bulabulin Maiduwa Bentonites that formed dispersive and poorly aggregated masses.

The SEM images of Beneficiated/Na activated Bentonites, shown in Figures 3 (b) to Figures 7(b) are said to be moderately dispersive with the addition of Na_2CO_3 which increased their dispersed tendencies. Some large flocs indicating weak interparticle bonding were also observed. These bonds are loosely held together and favours dispersion, this relatively conform with the findings of Erica, (2013). The flocs of the treated bentonite samples as shown in the SEM images in Figures 3 (c) to Figure 7(c) are not as large as those in raw samples, those in the

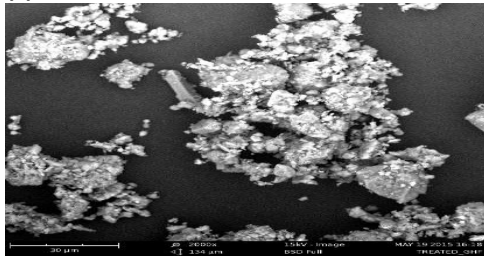
treated Garin Hamza, Pindiga and Sabongarin Ngalda images with the exception of Tongo and Bulabulin Maiduwa Bentonite that occupy the totality of the image and are slightly loose probably due to the effect of added poly anionic cellulose (PAC) during treatment. As such with the advancement of more, smaller flocs, stronger bonding occurs in the sample and the dispersive tendencies of the treated samples are slightly reduced compared to larger and dispersed flocs in Garin Hamza, Pindiga and Sabongarin Ngalda Bentonites.



(a) Raw Garin Hamza

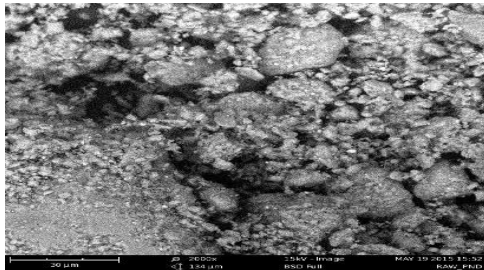


(b) Na activated Garin Hamza

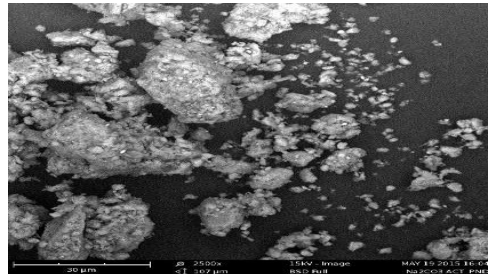


(c) Treated Garin Hamza

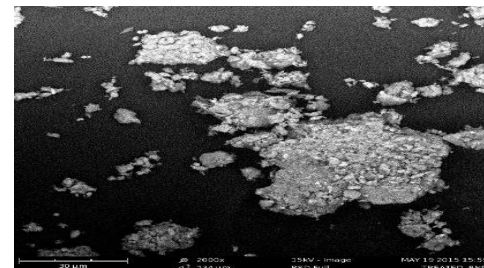
Figure 3: Comparison between SEM images of (a) raw, (b) Na activated and (c) treated Garin Hamza Bentonite



(a) Raw Pindiga

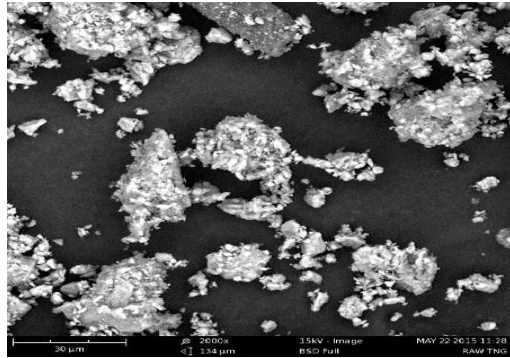


(b) Na activated Pindiga

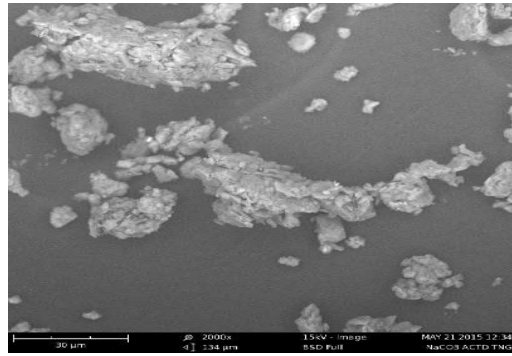


(c) Treated Pindiga

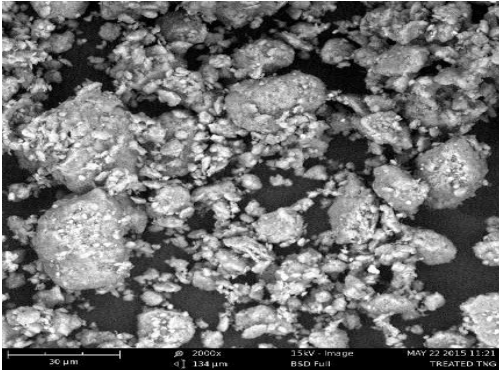
Figure 4: Comparison between SEM images of (a) raw, (b) Na activated and (c) treated Pindiga Bentonite



(a) Raw Tongo Bentonite

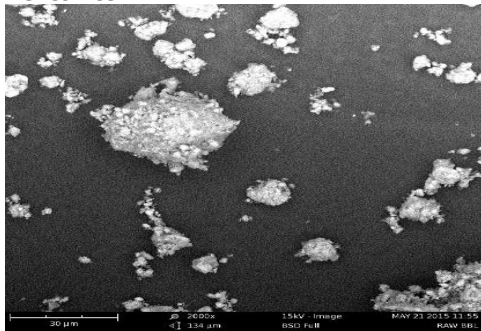


(b) Na activated Tongo Bentonite

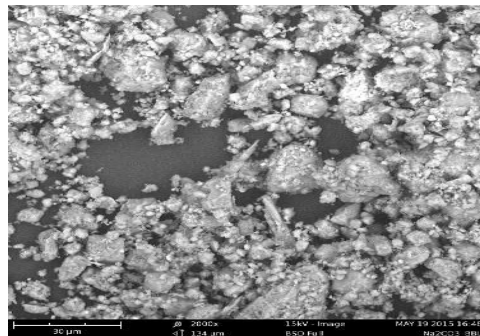


(c) Treated Tongo

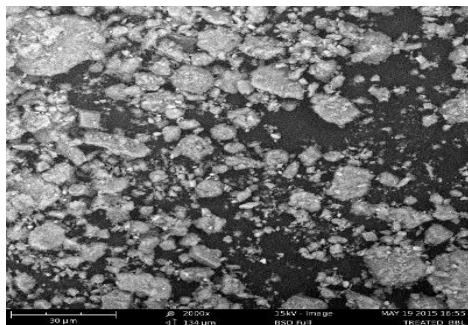
Figure 5: Comparison between SEM images of (a) Raw, (b) Na activated and (c) Treated Tongo Bentonite.



(a) Raw Bulabulin Maiduwa

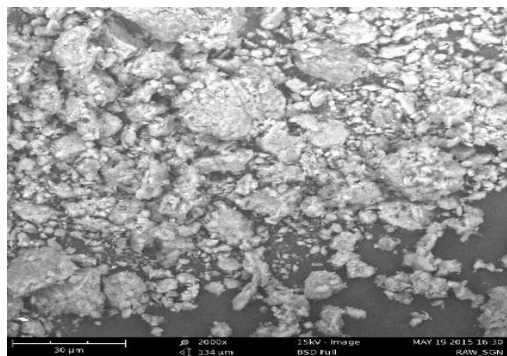


(b) Na activated Bulabulin Maiduwa

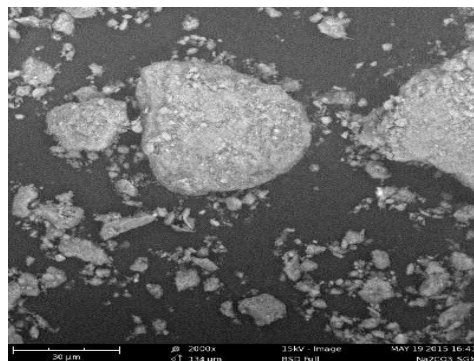


(c) Treated Bulabulin Maiduwa

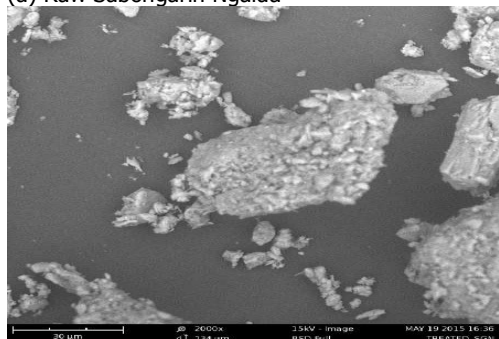
Figure 6: Comparison between SEM images of (a) Raw, (b) Na activated and (c) treated Bulabulin Maiduwa Bentonite



(a) Raw Sabongarin Ngalda



(b) Na activated Sabongarin Ngalda



(c) Treated Sabongarin Ngalda

Figure 7: Comparison between SEM images of (a) raw, (b) Na activated and (c) treated Sabongarin Ngalda Bentonite

In summary, the flocs observed in the SEM images in the beneficiated/Na activated and treated bentonite samples seems to be separate and deflocculated, they seem dispersed from one another. They seem fairly spread out which may indicate weaker bonds that characterised dispersive clay.

There are some rounded flocs but they seem small and dispersed rather than large and aggregated with one another. Few flocculated masses indicate a majority of weak interparticle bond forces in the clay sample. Weak forces cannot withstand the introduction of water into the system and thus, the soil is susceptible to dispersive behaviour (Erica, 2013).

CONCLUSION

The SEM microstructure images indicated that the Bentonite samples are generally moderately dispersive

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to dispersive with some large flocs which were apparently separate and dispersed from one another rather than located on the totality of the image, this property is more pronounced on the Na activated and the treated samples than in the raw samples, this could be due quartz removal and Na activation on the raw Bentonitic samples. Dispersive sample surfaces consist of loose wave-like flakes with no definitive mass structures observed on the treated samples due to added PAC to the samples.

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