



Studies on the Mineral and Chemical Characteristics of Pindiga Bentonitic Clay

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Abstract

Bentonite clay from Pindiga, Gombe State, Nigeria was investigated for its mineral content using X-ray diffraction technique. The chemical composition was also determined using X-ray fluorescence (XRF) technique. These determinations were carried out on the raw clay, wet beneficiated samples, calcined at 700°C, 750°C and 800°C as well as calcined samples acidified using sulphuric acid. The Pindiga raw bentonite was found to contain Ca-, K-, Na- and Mg-montmorillonite minerals with the calcium type being the predominant mineral. The calcium type also appeared to be the most thermally stable. Accessory minerals such as graphite, carbon, quartz and iron (III) oxide were detected. The quartz was completely removed by wet beneficiation while the carbonaceous matters burnt off completely on calcination to 800°C. The iron (III) oxide in the beneficiated sample calcined at 700°C appeared to react with the sulphuric acid treatment.

Introduction

Bentonite is light-colored clay that expands in water. It is principally used for oil drilling mud formulation, fillers for paper, pharmaceutical products, adsorbents and catalyst in the chemical process industries.

Bentonites are composed predominantly of the clay minerals montmorillonites, a sub-group within the smectites group. It is clay derived from deposits of weathered volcanic ash. A general chemical formula for montmorillonite is $m(\text{Mg}[\text{Si}_4\text{O}_{10}]_x[\text{OH}]_2)_x p([\text{Al,Fe}]_2)_x [\text{Si}_4\text{O}_{10}]_m$: $m:p = 0.8 - 0.9$. Depending on the nature of their genesis a variety of accessory minerals occur along with the montmorillonites. These may include quartz, feldspar, calcite, gypsum, dolomite, biotite, cristobalite, plagioclase and ferruginous compounds. There are three principal types of bentonite, namely:

1. natural sodium bentonite or sodium montmorillonite
2. natural calcium bentonite or calcium montmorillonite
3. sodium activated bentonite or sodium activated montmorillonite

There are also the potassium, magnesium and lithium types. Natural sodium bentonite as the name suggests, occurs with sodium as the predominant exchange cation. It is characterized by high swelling, high liquid limit and high thermal durability, and finds application as oil and gas drilling mud. Majority of bentonites occurring worldwide are of the calcium type. Calcium bentonite has lower swelling and liquid-limit values compared to natural sodium bentonite. It is used as a bleaching agent in cooking oil industries, and lubricant oil recycling, as a catalyst, absorber, filler, etc.

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Bentonite tuffs have been reported to occur in the Benue trough and around the Jos Plateau, but none of these was known to be associated with appreciable bentonite formation¹. Bentonitic clays also exist in the North-east quadrant of Nigeria (Borno, Yobe, Taraba, Gombe, Bauchi and Adamawa States) where a probable reserve of more than 700 million tones has been indicated. The work of Arabi et al² identified the bentonitic clay from Fika member of the Pindiga Formation in Upper Benue trough in north-eastern Nigeria to be Ca-based¹. Similarly, over 90 million tones have been reportedly found in Afuze, Ekpoma-Igueben road, Ovibiokhuan and Okpebho areas of Edo State. Some occurrences have also been reported in Abia, Ebonyi and Anambra States². The present level of consumption of bentonite in Nigeria as at 2007 was reported to be about 200,000 MT (for oil well drilling only); much of this was met by importation³.

A major difficulty in the processing of bentonites into commercially acceptable grade is their appearance. Bentonites are usually rich in organic matters, which colour them black or grey. As at now, only a few companies are known to produce bentonite from the local deposits in the country. There are ample opportunities for investors in the processing and development of bentonites to satisfy the growing domestic market and export. There is often the question as to whether the numerously reported bentonitic clay deposits in many parts of this country are true bentonites since true bentonite is derived from deposits of weathered volcanic ash and Nigeria has not been prone to volcanic eruptions in the past. It has however, been reported that Grin in 1972 redefined bentonite along a more general line as a clay body consisting essentially of montmorillonite minerals, regardless of origin or occurrence⁴. This paper is a report of an investigation carried out for Pindiga clay in Gombe State to establish its true mineral and chemical characteristics.

Materials and Methods

Chemical Reagents and other materials

The following chemical reagents and other materials were employed in the work carried out.

1. Pindiga bentonite clay
2. Concentrated Sulphuric acid (98wt%) Distilled water
3. Tap (potable) water

Instruments, Glassware and Equipment

The following instruments, glassware and equipment were used in the course of the investigation.

1. Weighing balances (Ohaus, model CS200, 0 – 200g), (0 – 100kg)
2. Mercury in bulb thermometer (0 – 100°C)
3. Plastic containers (50 -100 lt)
4. Glass funnel.
5. Beakers (150 - 500ml).
6. Measuring cylinders (50 -500ml).

¹ Raw Materials Research and Development Council (2007), Technical Brief on Mineral Raw Materials in Nigeria – Bentonite, Revised edn., RMRDC, Abuja.

² Arabi Suleiman Abdullahi, A. A. Ibrahim, M. A. Muhammad, M. Y. Kwaya and S. Mustapha (2011) Comparative Evaluation of Rheological Properties of Standard Commercial Bentonite and a Locally Beneficiated Bentonitic Clay from a Marine Deposit in Upper Benue Basin, Nigeria, *British Journal of Applied Science & Technology* 1(4): 211-221, 2011

³ Ibid

⁴ Ibid

7. Round bottom flasks (250, 500ml)
8. Ceramic crucibles (70ml, 250ml)
9. Desiccators
10. Clay pots (8 lt)
11. Electric ovens (NYC, model 101, 25° - 220°C), (Nabertherm B150 model, 25° - 650°C)
12. Nabertherm C250 Electric furnaces (1400°C)
13. Ceramic and wooden mortars and pestles
14. Stainless steel spatula
15. Digital stop watch
16. Hydraulic press (50 tones)
17. X-ray diffraction (XRD) machine (Stchmabzu model 6000).
18. X-ray fluorescence (XRF) machine (Pananalytical, minipal 4).

Experimental Procedure

The experiments carried out include the beneficiation of the raw bentonite sample, calcination of the beneficiated bentonite, acidification of the calcined bentonite, XRF analysis of the bentonite samples and XRD analysis of the bentonite sample. Step by step accounts of the procedures followed are as follows:

Beneficiation of the Raw Bentonite - Raw bentonite sample obtained from a deposit in Pindiga, Gombe State was collected. 9.5kg of the clay was weighed and crushed down from lumps to coarse powder form using wooden mortar and pestle. The coarse powder was soaked in 95 litres of water in a plastic container and the mixture was blunged (stirred) for 3 hours at room temperature. The stirred mixture was then allowed to remain in the container for 24 hours for the coarse quartz impurities to sediment to the bottom leaving colloidal solution of bentonite at the top. The colloid bentonite was collected and separated from the quartz sediments and sieved through a 230 mesh Tyler sieve (63µm sieve opening) to further remove coarse impurities. The clay obtained was allowed to settle and thickened in clay pots. The thicken clay was put in a filter bag and pressed under a hydraulic press to squeeze out the water. The resulting cake was dried in an oven at 300°C to constant weight, broken down to powder and stored in a large polyethylene bag for the subsequent experiments. The beneficiation process took 19 days to complete.

Calcination of the Beneficiated Bentonite 150g of the beneficiated clay was fired gradually in an electric furnace to 700°C and soaked at that temperature for 3 hours. The calcined clay was allowed to cool and analyzed for chemical and mineralogical compositions using AAS and XRD. The calcination was repeated for the temperatures of 750° and 800°C. The calcination temperatures were selected based on the fact that the hydroxyl group (chemically combined water or water of hydration) in montmorillonites structure gets destroyed at temperatures between 600°C and 700°C as shown by the differential thermal analysis pattern of Wyoming bentonite (Figure 1)⁵

Acidification of the Calcined Bentonite 30g of the clay at each calcined temperature was treated with sulphuric acid using both dry and wet methods. The dry method involved weighing the concentrated sulphuric acid (98wt%) at an acid:dry clay weight ratio of 0.3:1.0 and mixing them dry and treated at a temperature of 95°C for 8 hours. Other preparations were made, but this time the bentonite was soaked in 6M sulphuric acid solution and stirred

⁵ Sand, I. B. and Crowley, M. S. (1960), Comparison of natural bentonite with its synthetic analogue

for 5 minutes. The clay was then filtered, dried and treated at 95°C for 8 hours. Samples of the materials obtained were analyzed for their chemical and mineralogical compositions.

XRF Analysis of the Bentonite Samples XRF analysis was carried out on the bentonite samples at the National Geosciences Research Laboratory (NGRL), Kaduna of the Nigerian Geological Survey Agency for their chemical compositions. Prior to this the true powder density, the pH and the loss on ignition were determined at the PTDF Chair laboratory in the Department of Chemical Engineering, Ahmadu Bello University, Zaria. The true density measurement was carried out using the Archimedes method while the loss on ignition was determined following the ASTM standard procedures.

XRD Analysis of the Bentonite Samples XRD analysis was carried out on the raw, beneficiated, calcined and acidified bentonite samples at the National Steel Raw Materials Exploration Agency (NSRMEA), Kaduna using Cu α radiation at a scan speed of 4°/min 2 θ following standard procedures.⁶

Results and Discussion

Physical and Chemical Compositions of the Pindiga Bentonite

The results of the physical and chemical analysis carried out on the Pindiga bentonite, both raw, beneficiated, calcined and acidified samples are presented as Table 1.

Table 1: Physical and Chemical Characteristics of Pindiga Bentonitic Clay

SN	Parameter	Raw Bentonite		Benef.	Calc750C	Calc800C	Acidified
		Measured Value	Typical Lit. Value	Measured Value	Measured Value	Measured Value	Wet 800C Measured Value
1.	pH	8.0	8.0-10.0*	7.5	ND	ND	ND
2.	Density, g/cm ³	2.58	2.5–2.8*	2.45	ND	ND	ND
3.	Loss on Ignition, wt%	6.46	NA	6.63	ND	ND	ND
4.	Al ₂ O ₃ , wt%	14.00	13.33**	15.00	17.10	15.90	11.00
5.	SiO ₂ , wt%	43.60	69.00**	46.90	49.50	48.60	52.40
6.	Fe ₂ O ₃ , wt%	26.54	2.09**	24.15	22.15	22.28	15.34
7.	K ₂ O+Na ₂ O+MgO wt%	3.52	NA	3.71	3.54	3.67	3.06
8.	Na ₂ O, wt%		1.93**				
9.	CaO, wt%	2.46	2.83**	2.00	1.83	1.90	1.55
10.	MgO, wt%		3.38**				
11.	MnO ₂ , wt%	0.38	NA	0.18	0.17	0-.17	0.07
12.	TiO ₂ , wt%	2.06	NA	2.15	1.98	2.03	2.29
13.	SO ₃ , wt%	1.00	NA	-	-	0.09	10.10

ND – Not Determined

*Na-bentonite

**Ca-bentonite NA-Not Available

⁶ Klug, H. P. and Alexander, L. E. (1974), X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 2nd Edn., John Wiley & Sons, New York.

It was observed from the table that the pH and density values for the raw bentonite were within the range of literature values for typical bentonite. The true powder density of the beneficiated sample was a little lower than for the raw bentonite, probably due to removal of denser accessory minerals. The loss on ignition of the beneficiated clay was less than for the raw sample. This was again understandable bearing in mind that anhydrous substance and organic matters were removed during the beneficiation.

The chemical composition showed that the alumina content of the raw bentonite was 14.00wt%, which was in agreement with the literature value of 13.33wt% for Ca-bentonite. The Al_2O_3 content increased to 15.00wt% for the beneficiated sample. The value further increased for the calcined samples. On wet acid treatment the value decreased significantly to 11.00wt%, apparently due to the acid dealumination of the bentonite. The silica content was 43.60wt% for the raw sample and increased to 46.90wt% for the beneficiated sample. A decrease was expected since quartz was removed during beneficiation. Analytical error may have been responsible. There were very high concentrations of Fe_2O_3 in all the samples. This explains the brownish colour of the raw bentonite and the reddish colour of the calcined samples. Calcium oxide was present in moderate concentrations typical of Ca-bentonite while low concentrations of manganese dioxide were recorded. K_2O , Na_2O and MgO could only be determined as a group by the XRF machine. Their total content was low for all the samples; the raw sample, for example had value of 3.52wt% compared to the literature value of 5.31wt% (1.93 + 3.38wt% for Na_2O and MgO respectively) for Ca-bentonite.

XRD Patterns of the Pindiga Bentonite

The XRD patterns of the raw, beneficiated, calcined and acidified Pindiga bentonite are presented in Figures 2-4. In Figure 2 the diffractographs show the characteristic peaks of montmorillonites in both the raw and beneficiated samples. In the raw bentonite both the calcium, sodium, potassium and magnesium montmorillonites seemed to be present. After beneficiation the peaks for calcium montmorillonite became more prominent while the others became less prominent. Figure 3 shows the diffractographs for the calcined samples. After calcination at 700°, 750° and 800°C the peaks for sodium montmorillonite disappeared completely while only one peak for Mg-montmorillonite could be detected. The peaks for K-montmorillonite also became less prominent with firing. It is either that the hydroxyl group (from the water of hydration) in the Na-, Mg- and K-montmorillonites was getting destroyed faster than the Ca-montmorillonite at those temperatures or that the predominance of the Ca-montmorillonite over the others was overwhelming. It was however, clear that the bentonite was more of the Ca- type.

Carbon, graphite, quartz and iron (III) oxide seemed to be present as accessory minerals. After beneficiation much of the graphite, carbon reduced while the quartz disappeared as corroborated by the chemical compositions. This suggested that the beneficiation process was effective in the near total removal of the quartz and reduction of the carbonaceous constituents. The iron content seemed to be high with the sharp peak recorded at d-spacing of 3.66Å (2θ of 24.3°) but did not seem to be affected much by the beneficiation process. On calcination the graphite and the carbon burnt off; and after firing to 800°C they had completely burnt off.

Figure 4 shows diffractographs for the samples calcined and acidified by the dry and wet methods. The peaks for the iron (III) oxide in the sample calcined at 700°C and acidified by wet method had reduced considerably while a new peak appeared at d-spacing value of 9.717Å (2θ of 9°). It is believed that a new crystalline insoluble iron-sulphur compound had

formed, but the JCPDS files available to this work could not identify the compound. This phenomenon was not pronounced for the sample calcined at 800°C and acidified by wet method, which suggested that the 800°C heat treatment had rendered the system less reactive and could no longer be severely attacked by the sulphuric acid. It was observed that only a slight reaction occurred between the iron (III) oxide and the sulphuric acid in the calcined samples acidified by the dry method. The dry method obviously did not permit proper penetration of the acid into the interior of the bentonite particles while the wet method allowed more intimate contact.

Conclusions

The following conclusions may be made from the foregoing discussions:

1. The chemical composition of Pindiga raw bentonite sample from Gombe State showed moderate contents of Al_2O_3 , SiO_2 and CaO while the Fe_2O_3 content was very high at 26.54wt%. Wet acid treatment of the bentonite with sulphuric acid caused dealumination of the clay.
2. XRD investigation showed that the bentonite sample contained the Ca-, K-, Na- and the Mg-montmorillonites minerals with the calcium type being the dominant mineral. The calcium type also appeared to be more thermally stable than the rest.
3. The accessory minerals that could be detected from the XRD pattern were graphite, carbon, quartz and ferric oxide. The quartz was completely removed by wet beneficiation while the carbonaceous matters burnt off completely on calcination to 800°C.
4. The ferric oxide content was significantly attacked by sulphuric acid treatment on the bentonite sample calcined at 700°C.

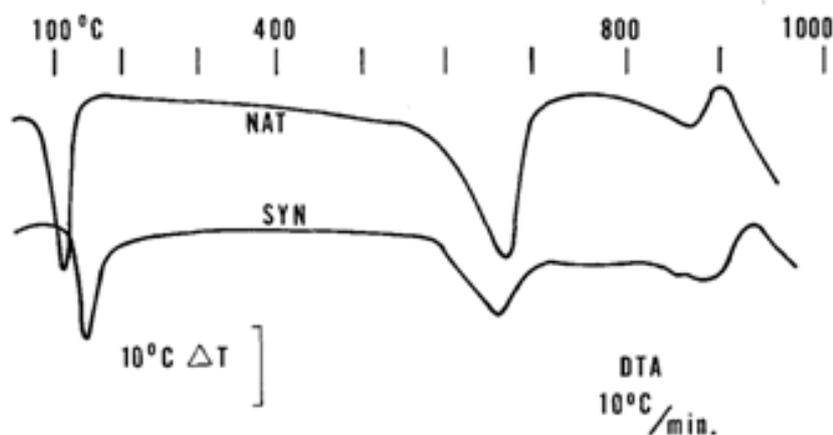


FIGURE 1. — Differential thermal analysis patterns of Wyoming bentonite (NAT) and its synthetic analogue (SYN). (I. B. Sand, 1960).

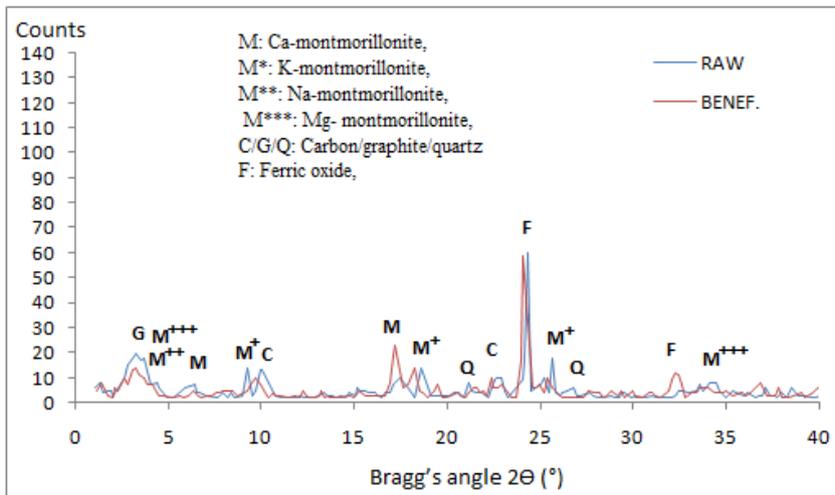


Figure 2: XRD Patterns of the Raw and Beneficiated Samples

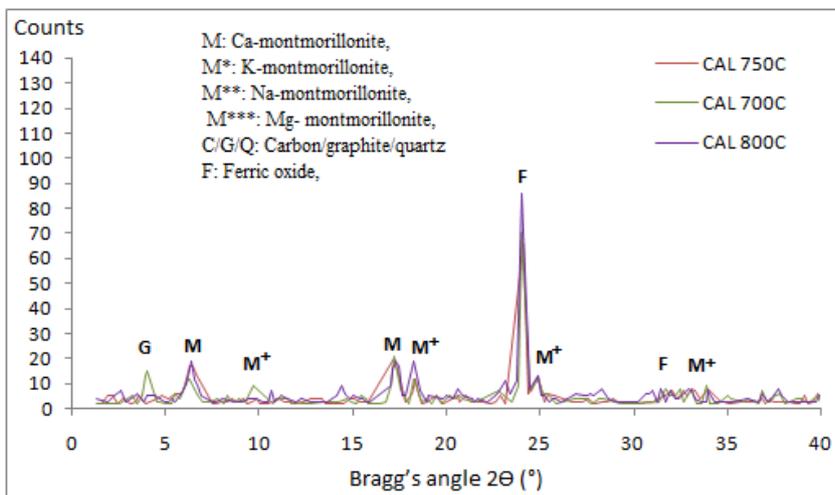


Figure 3: XRD Patterns of the Beneficiated Bentonite Samples Calcined at Various Temperatures

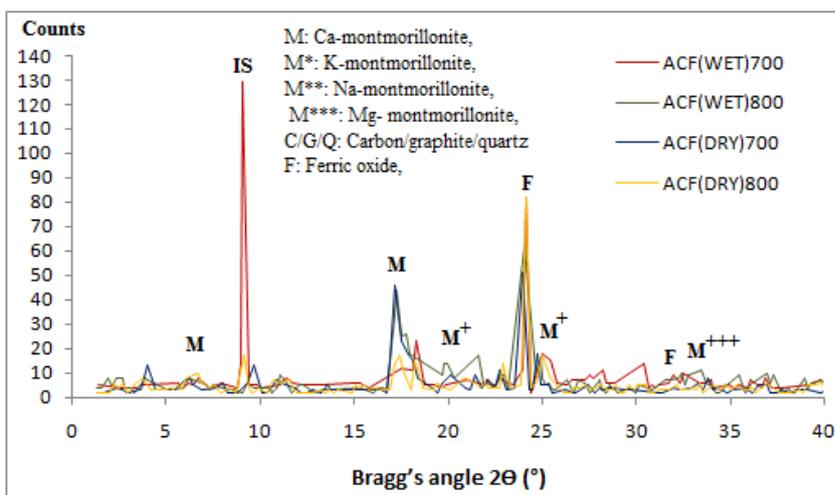


Figure 4: XRD Patterns of Calcined and Acid Treated Bentonite Samples