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Iron Removal from Local Bentonitic Clay and Its Effect on Clay Rheology

By

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Abstract

The performance of treated clays (Bentonite) in oil and gas well drilling is affected at high temperature and pressure to some extent by level of concentration of iron present in the drilling mud. This study is aimed at improving the quality of clay from Pindiga Formation in northeastern Nigeria through iron (Fe) content reduction without compromising its structural, rheological and other physical properties. The Pindiga Bentonitic clay is intended for beneficiation for use in oil well drilling. Iron was removed from the clay using oxalic and hydrochloric, and the effects of the procedure on clay structure have been investigated. The results indicate that the optimum iron removal with mild structural effects was obtained using 1M hydrochloric acid at 70°C. This is indicated by slight change on the infrared Al-O-Al peak intensity (36.49 and 33.07) of the Fourier Transformed Infra-Red (FTIR) spectra and the change in iron concentration (4.57% and 2.54%) observed from results Instrumental Neutron Activation Analysis (INAA) analysis conducted before and after the iron removal, respectively. The use of hydrochloric and oxalic acid produced the most effective iron removal procedure using 1M and 1.8M, respectively, at 70°C, and less effect on the clay structure than obtainable using more concentrated acid solution at lower temperature. This showed that the use of 1M hydrochloric acid at 70°C can effectively reduce the iron contents in clays with little effect on the crystal structure as indicated by the IR spectrum, especially when iron concentration in such clay is less than 15% above what is obtainable in the API grade Bentonite as is the case of the studied clay.

Keywords: Clays; Structure; Nigeria; Stability; Rheology

1. Introduction

Drilling for oil and gas constitute about eighty percent (80%) of the total well cost. Oil and gas well drilling has evolved from vertical, inclined, horizontal to sub-sea and deep-sea drilling. These specialized drilling processes require specialized drilling fluids to fulfill the objectives. Since reservoir type and the drilling process adopted to exploit the reservoir fluid is unique, the drilling fluid has to be customized to suit the drilling process and reservoir conditions[1].

Nigeria is the largest oil producer in Africa and was the world's fourth leading exporter of liquefied natural gas (LNG)[2]. Not a single of these Oil wells are drilled without the use of

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[1]Subhash N. Shah, Ph.D., P.E., Narayan H. Shanker, and Chinenye C. Ogugbue (2010). Future Challenges of Drilling Fluids and Their Rheological Measurements, American Association of Drilling Engineers, AADE-10-DF-HO-41

[2] United State energy information, (2013). Independent Statistics and Analysis, http://www.eia.gov/countries/cab.cfm?fips=ni

Bentonite. Hundreds of millions of dollar is being spent by the oil companies on importation of Bentonite from overseas while Nigeria has enough reserve of Bentonitic clay deposit all over the country that requires a little beneficiation to meet the required standard for use as a drilling mud in oil and gas well drilling operations. This will translate into retaining the large sum of money spent on importation of foreign Bentonite, create employment opportunities, bring external investment and boost the country's economy[3].

Bentonite is a clay 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 other species of quartz. The special properties of bentonite are its ability to form thixotrophic gels with water, an ability to absorb large quantities of water, and a high cation exchange capacity.

The properties of bentonite are derived from the crystal structure of the smectite group, which is an octahedral alumina sheet between two tetrahedral silica sheets. Depending on the dominant exchangeable cations present, the clay may be referred to as calcium bentonite or sodium bentonite, the two varieties exhibiting markedly different properties and thus uses.

The functions of drilling fluid encompass cleaning the hole, stabilizing the strata drilled, controlling subsurface pressures, sealing fluid losses, enhancing drilling rates and protecting potential production zones while conserving the environment in the surrounding surface and subsurface.

The thermal stability of drilling fluid is affected at high temperature and pressure (down-the-hole conditions) by the presence of iron, thus, referred to as impurity. Therefore, this study is aimed at finding the best procedure for reducing as much as possible the iron concentration of a locally beneficiated clay form Pindiga Formation in northeastern Nigeria with/without little or no damage to its structure using oxalic and hydrochloric acids at different temperatures.

Carter et al[4] proposed the name Pindiga Formation for "Calcareous beds" and "clay shale" previously described by Barber[5]. It makes up the greater part of the Upper Cretaceous deposits in the Upper Benue Trough[6]. Geology of Pindiga Formation is detailed in Zaboski et al[7] after extensive work on the Pindiga Formation and recognized five Members namely; Kanawa, Gulani, Deba Fulani, and Fika Members. Detail on rheological and other physical properties of Pindiga clay is provided in Dewu et al and Dewu et al[8].

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[6] Zaboski, P., Ugodulunwa, F., Idornigie, A., Nnabo, P and Ibe, K. (1997). Stratigraphy and Structure of the Cretaceous Gongola Basin: North-Centers Researches *Exploration-Production ELF- Aquitaine*. 21: 153-154.

[7] Ibid

[8] Dewu, B. B. M; I. I. Funtua; M. O. A. Oladipo; A. S. Arabi; I. A. Mohammed-Dabo; A. M. Muhammad and I. Hamidu, (2011) Evaluation and Beneficiation of Bentonitic Clays from Pindiga Formation in Benue Trough. *American Journal of Engineering and Applied Sciences* 4(4): 497-503; and Dewu, B. B. M; Arabi, S.A; Oladipo, M. O. A; Funtua, I.I; Mohammed-Dabo, I. A. and I. Hamidu. (2011) Improvement of Rheological Properties of Bentonitic Clays Using Sodium Carbonate and a Synthetic Viscosifier. *International Archive of Applied Sciences and Technology*, Vol. 2 [2]: 43-52

This study is aimed at determining the mineralogy of the samples and that of API grade standard clay, the concentrations of Fe, Ca, Ti, Al and Mg in sample before and after acid treatment (targeting the iron removal), determine the implications of acid treatment (iron removal) on the concentrations of other associated elements (Fe, Ca, Ti, Al and Mg) and most importantly to determine the extent of iron removal and its effects on the clay structure in comparison with the API grade Bentonite using X-Ray Diffraction (XRD) for mineral phase determination, Instrumental Neutron Activation Analysis (INAA) and Multi-analyte photometry for elemental determination in both liquid and solid phases respectively, and Fourier transformed Infra Red Spectral analysis for evaluation of Al-O-Al peak intensity for structural study of the clay before and after the treatment in order to evaluate the effect of acid treatment on the clay crystallography. Studies on clays elsewhere have been conducted using different formulation and technique.[9] Others are those by Hosseini et al[10] and Lee et al.[11]

2. Materials and Methods

Raw representative clay sample was obtained along exposed section of River channel around Pindiga Town in northeastern Nigeria. Surface of the exposure was carefully removed and fresh sample was taken, stored in pre-cleaned polyethylene containers and brought to the laboratory for the study. The sample was dried at room temperature, crushed to less than 125µm particle size and dissolved in water (clay-water- ratio 2:5) by stirring until no lumps were present. The mixture was allowed to stay for 48hrs after which three distinctive layers of supernatant liquid, clay and silica were formed (Fig. 2).

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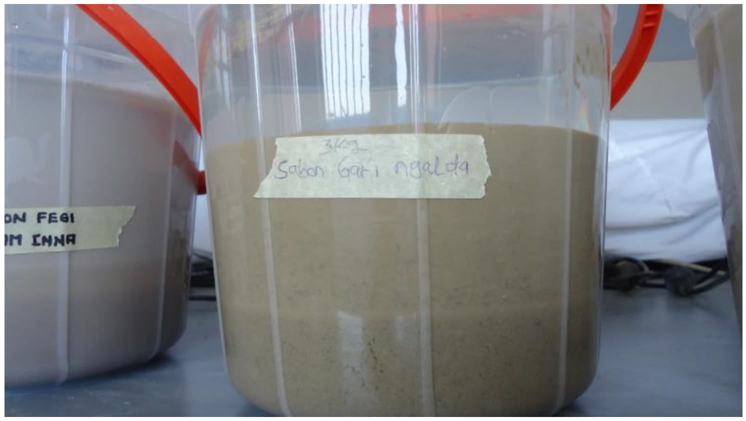

Fig. 1: Photograph showing three distinct layer of the clay of supernatant liquid, clay and silica formed (bottom) clay.

The supernatant liquid was removed by suction while the middle layer (clay) was set on trays and oven dried at $60^{o}C$. The dried clay was then crushed to 125µm particle size.

2.1 Iron removal from clay

Two concentrations of hydrochloric acid (*HCl*) acid solutions (4M and 1M) and a 1.8M oxalic acid solution were prepared and 300mL of each was measured in to a separated 400mL glass beaker. The acid solutions were heated on a hotplates equipped with magnetic stirrer rotating at 150rpm. The 4M HCl portion was thermostated at $50^{o}C$ while the 1M HCl and 1.8M oxalic were thermostated at $70^{o}C$ during which 10g of clay was dissolved in each acid solution and the heating was maintained for 6 hours as in Mitchell and Mackenzie.[12]

At the end of the heating, the solution was decanted and the supernatant liquid collected. This was followed by washing of the clay until the pH rises above 5 after which it was oven dried at $60^{o}C$ to ensure that the clay structure is not thermally degraded. The final sample (acid leach clay) was then analyzed for final elemental composition using instrumental Neutron Activation Analysis (INAA) and to evaluate the Al-O-Al peak intensity using Fourier transformed Infra Red Spectral analysis (FTIR, Aluminum peak intensity) for structural alteration evaluation. Also, iron concentrations in liquid used in the treatment of the clay before and after acid treatment was determined. Also, mineralogy of the sample (Clay sample and API grade Bentonite) was determined using X-ray diffraction method.

Instrumental Neutron Activation Analysis (INAA) was employed in the elemental analysis of the raw Pindiga clay, API grade Wyoming clay and samples generated after acid leaching of the local clay. NIST Standard Reference Materials (SRM) 1633b (coal fly ash) and 2710 (Montana soil) were used to assess the quality of the analysis and the results are shown in Table 1.

Standard Reference Material (SRM) values from this work agree with the certificate value to within 95% confidence interval except for calcium in NIST 1633b (Table 1). Mg, Ca and Ti in

[12] B. D. Mitchell and R. C. Mackenzie (1954) Removal of free iron oxide from clays. Soil Sci. 77: 173 – 184

NIST 2710 (Table 1) were not reported due to the uncertainty generated by excess activity of manganese in the SRM.

Table 1: Standard Reference Material (SRM) values from this work and their certificate values

ELEMENT	NIST1633b (This Work)	NIST1633b (Certificate value)	NIST 2710 (This Work)	NIST2710 (Certificate value)
Mg	4688 ± 877	4820 ± 80	-	8530 ± 420
Al	145500 ± 1164	150500 ± 600	66210 ± 530	64400 ± 800
Ca	11310 ± 1312	15100 ± 600	-	12500 ±300
Ti	8014 ± 561	7910 ± 140	-	2830 ± 60
Fe	76130 ± 457	77800 ± 2300	34540 ± 345	33800 ± 100

Note: All concentrations are in ppm

3. Results and discussions

The results presented here are those of mineral phase identification (XRD) which clearly identified major mineral constituent of both clay sample and that of the standard (API grade Bentonite), Elemental Neutron Activation Analysis results showing all the major element that can be effected by the procedure to be able to track enrichment or depletion at the end of the study.

3.1 Characterization of sample using X-Ray Diffraction

X-Ray Diffraction analysis of both Pindiga clay and API grade samples (Fig. 1a and 1b) revealed that the mineral phases present in accordance with their abundance are:

Pindiga: Quartz > Montmorillonite > Kaolinite

API Grade Bentonite: Montmorillonite > Barite > Almandine > Quartz

This indicates that the API grade Bentonite is dominantly made of Montmorillonite and has been blended with Barite powder possibly to improve its weighing capacity. The Pindiga clay on the other hand has quartz as its dominant mineral with some Ca-base Montmorillonite and kaolinite (Fig. 1). This also means that for the Pindiga clay to attain the standard required for use as drilling mud, silica content must be reduced followed by beneficiation either through sodium activation or other methods.

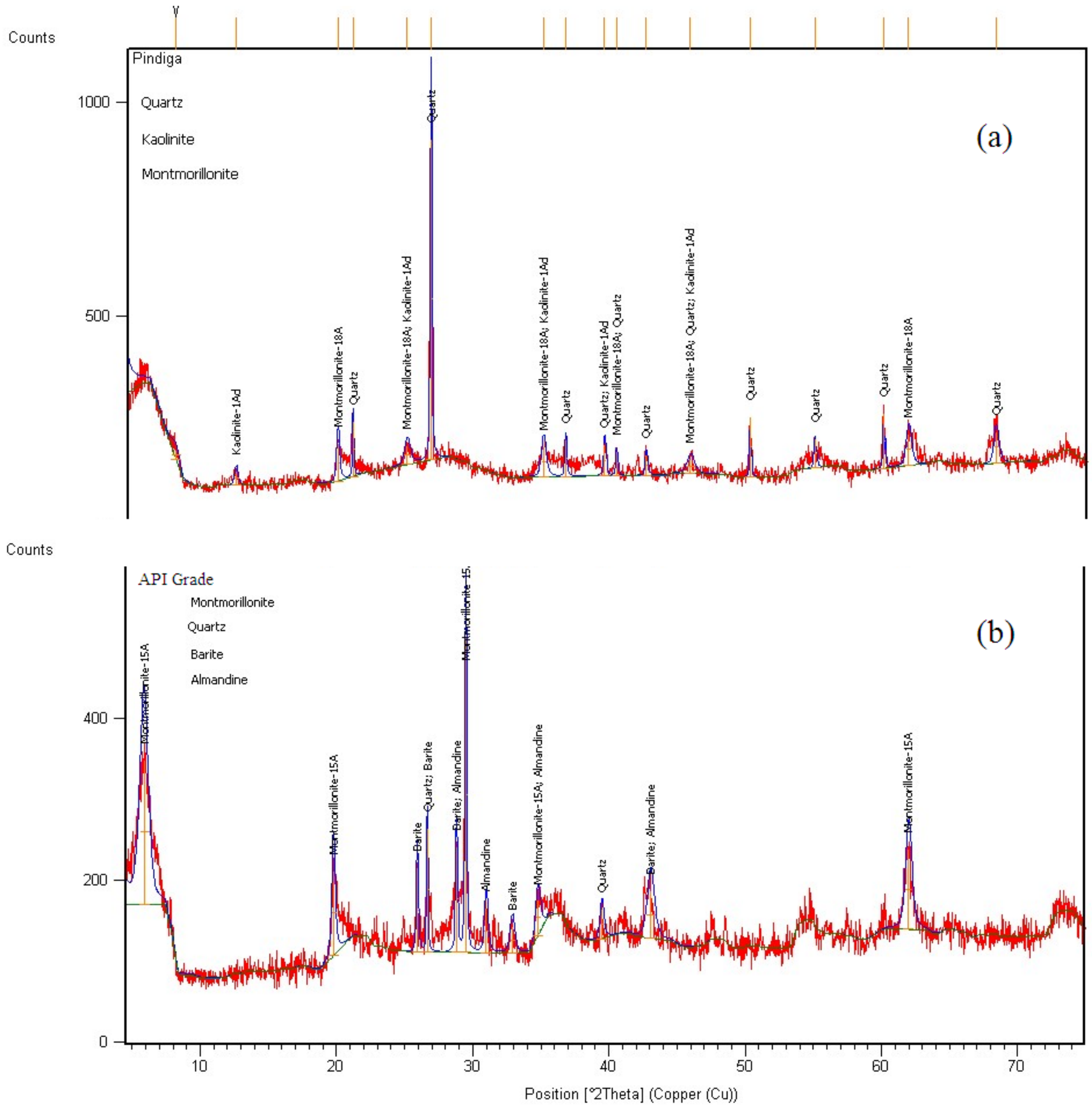

Fig. 1: X-Ray Diffraction spectrum of (a) Raw Pindiga clay and (b) API grade Bentonite

3.2 Elemental concentrations of Pindiga clay and API grade Bentonite

The concentration of Mg, Al, Ca, Ti and Fe in Pindiga, API and treated portion of the samples is presented in Table 2. The results clearly indicate that treatment had effects on concentration of all the elements. For example, the treatment of Pindiga clay with 4M at 50°C and 1M at 70°C of HCl had reduced the Ca concentration to a level below detection (BDL) (Table 2) while treatment with oxalic acid reduced this from 5421 ± 1068ppm to 5351 ± 894ppm. High concentration of Ca in clay intended for drilling affect its rheological property negatively hence, the need for activation of Ca-base clay with $NaCO_3$ to replace Ca with Na in the clay structure, thus, improving its rheology.

Table 2: Concentration of Major element in the samples as determined by INAA

Element	Raw Pindiga	4M 50 HCl	1M 70 HCl	1.8M 70 Oxalic	API grade Bentonite
Mg	4554 ± 63.3	6757 ± 64	4412 ± 81	4022 ± 825	7758 ± 79.1
Al	101400 ± 1216	106800 ± 1068	81740 ± 736	84750 ± 339	69430 ± 694
Ca	5421 ± 1068	BDL	BDL	5351 ± 894	35610 ± 2492
Ti	6867 ± 522	8224 ± 699	5473 ± 520	7342 ± 418	3382 ± 632
Fe	45690 ± 368	33780 ± 304	25360 ± 279	26050 ± 261	33920 ± 339

BDL=below detection limit

The study showed that raw Pindiga clay had iron concentration 34.7% more than API grade bentonite. After acid leaching of the raw Pindiga clay with 4M HCl, 1M HCl and 1.8M oxalic acid, the iron concentrations were reduced 26%, 44.5% and 43% respectively. These results in the acid leached clays having lower iron concentration than the API clay (0.4, 25.3 and 23.2% respectively). Calcium concentration was found to be 5.6 times greater in API grade bentonite than in Pindiga clay, while aluminum is 31.5% lower. Mild acid and higher temperature (70^{o}C) combination reduces iron concentration most significantly. However, the combination also removes more aluminum and magnesium.

3.3 Fourier transformed Infra-Red (IR) Spectrum analysis

The IR spectrum of API grade Bentonite shows similar peak intensities for Si-O-Al, Al-Mg-OH and Al-O-Al with raw Pindiga clay (Fig. 2). API grade Bentonite failed to show SiO_2 (Silica) absorbance at 795 and 915 cm^{1} (Fig. 3). This also support the X-ray diffraction spectra, that the raw Pindiga clay contains more quart than montmorillonite. The results also show decrease in silica intensity especially when leaching was done with oxalic acid.

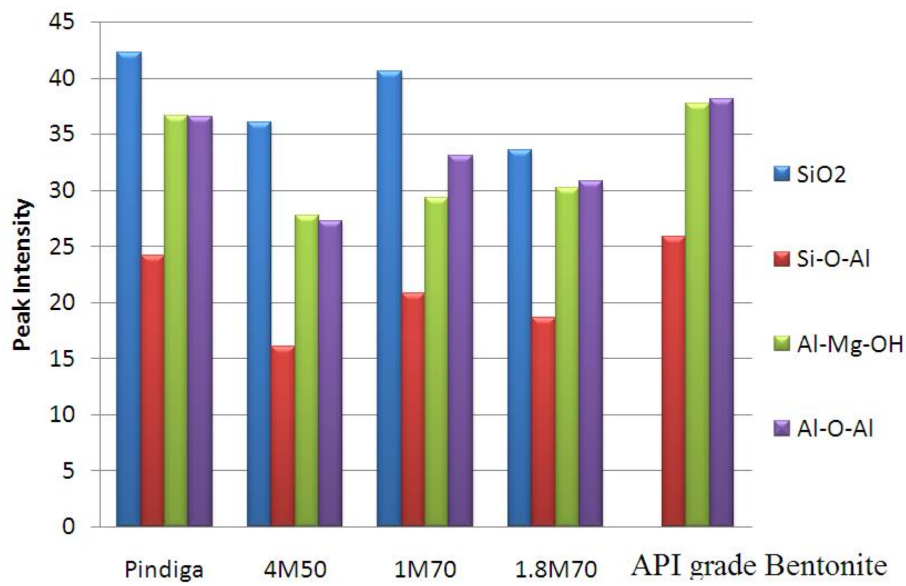

Fig 2: Infrared spectroscopy Iintensities of Bentonitic clay bonds

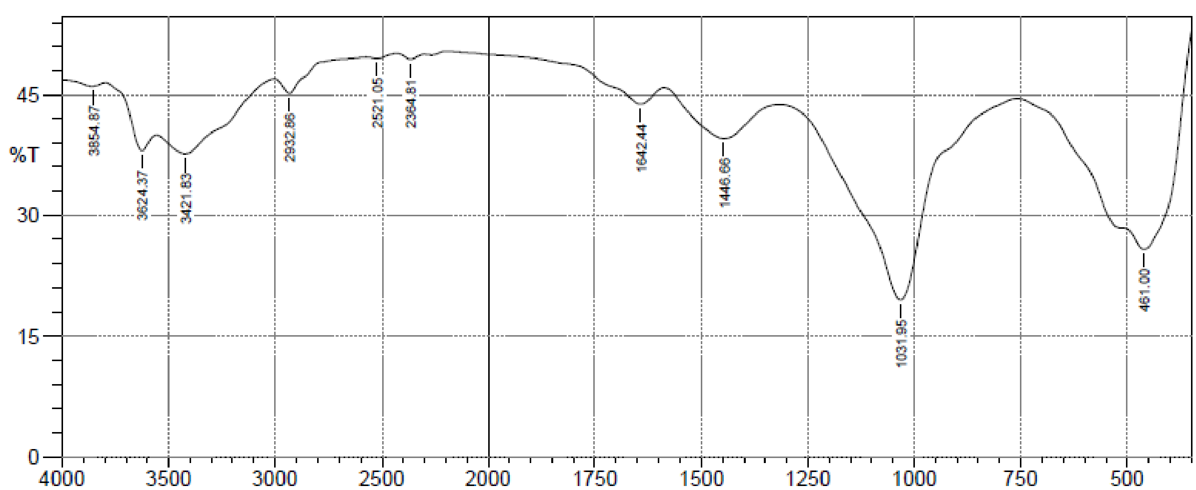

Fig 3: Infrared spectrum of Pindiga clay

3.4 *Clay treated with 4M HCl at 50^oC*

Treatment of Pindiga clay with 4M HCl solution at 50^{o}C showed an increase in the concentration of Mg, Al and Ti by 48.4, 5.3 and 19.8%, respectively, while Iron concentration was reduced by 26.1% (Table 2).

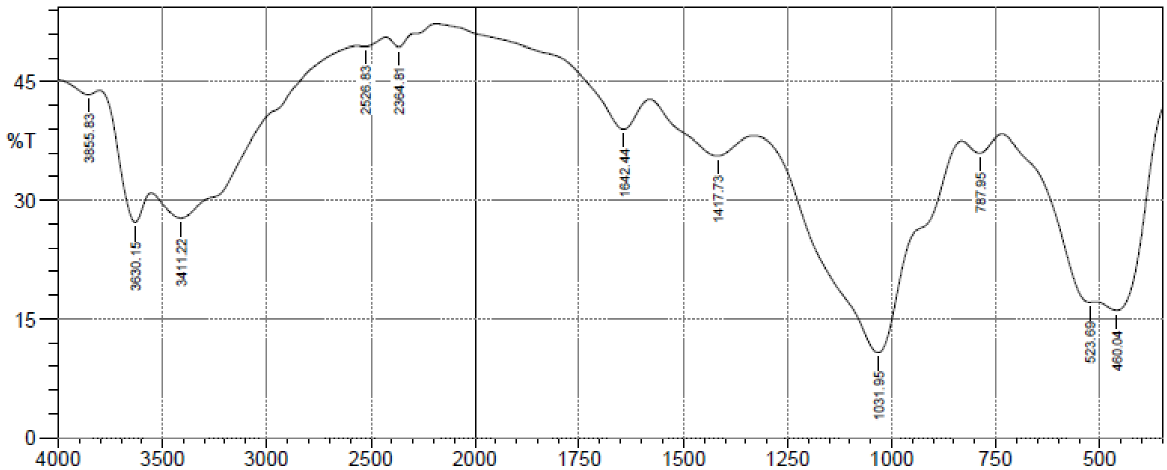

Fig 4: Infrared spectrum of Pindiga clay leached with 4M HCl

The IR spectrum of the sample showed 24.3% decrease in the intensity of Al-Mg-Al peak at 3420 cm^{1}. On the other hand, Si-O-Al and Al-O-Al peaks at 2940 and 3620 cm^{1} showed intensities decrease at 33.5 and 25.4% respectively (Fig. 4).

The decrease in the intensity of Al compound peak by FTIR indicates a relative degradation of clay structure, while the increase in aluminum concentration as indicated by INAA result indicates that, relative to other clay constituents, Al is slightly solvated and removed by acid treatment during washing.

3.*5 Clay treated with 1M HCl at 70^{o}C*

In contrast to 4M acid leaching, the concentration of all the elements under study reduced and in some cases, the reduction was significant, especially, Mg by 3.1%, Al by 19.4%, Ti by 20.3% and Fe by 44.5%.

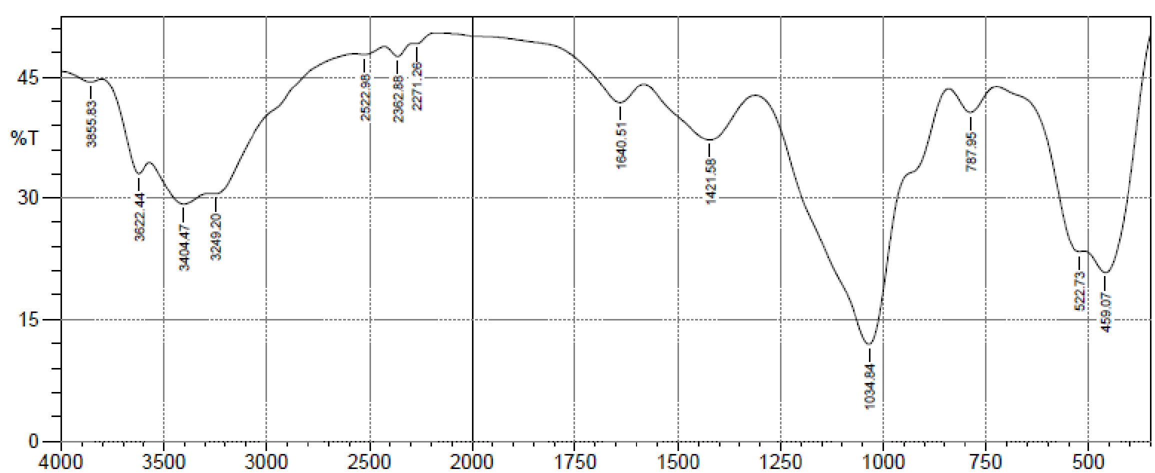

Fig 5: Infrared spectrum of Pindiga clay leached with 1M HCl

The FTIR spectrum indicates that the 1M acid leaching is milder on the clay structure. Al-Mg-OH peak shows 20.2% decrease in intensity while the Si-O-Al and Al-O-Al peaks (Fig. 5) show 14.0 and 9.4 % decrease.

3.6 *Clay treated with 1.8M Oxalic Acid at 70°C*

Treatment with oxalic acid provides a result similar with that of INAA as 1M HCl treatment at 70°C except that Ti, had 6.9% increase.

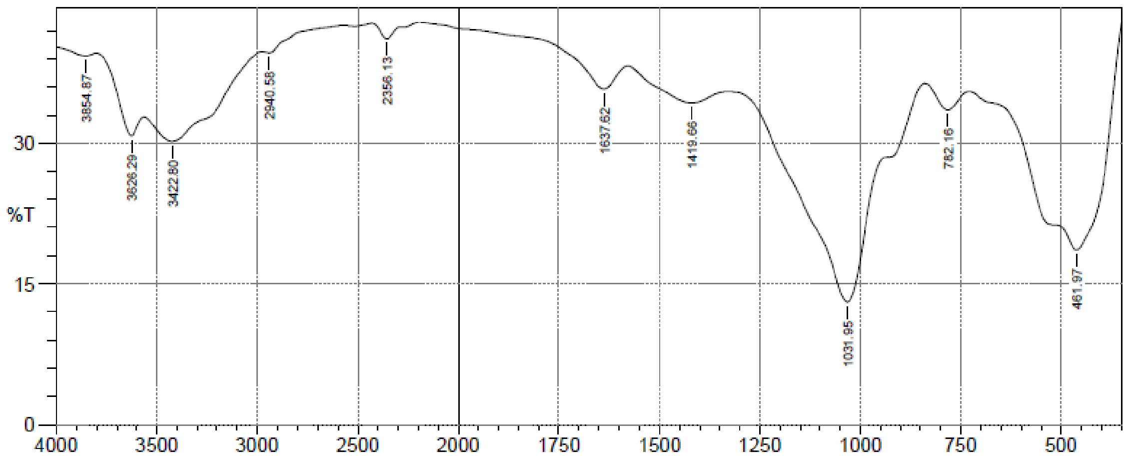

Fig 6: Infrared spectrum of Pindiga clay leached with 1.8M oxalic acid

Similarly, the FTIR result (Fig. 6) reported peak intensities similar to 1M HCl leaching. However, SiO_2 peak reported 20.8% decrease, which is closer to the value of 4M HCl leaching.

3.7 *Effect of Iron removal on Clay Rheology and CEC*

The clay mineral, Montmorillonite, is responsible for the excellent properties of bentonite. It is an aggregate of lamellar platelets, with each platelet consisting of two tetrahedral alumino-silicate layers and a central octahedral alumina layer, with interposing water and exchangeable cations sandwiching the layers. Hydration of the exchangeable cations is the main cause of the bentonitic swelling, which gives it high correlation between shear stress and shear rate, and defining it use as a drilling fluid (lubricant).

Acidity negatively affect water uptake in clay and consequently, swelling and viscosity of the clay while removal of iron and degradation of silicate have positive effect. Plastic viscosity (PV) and Yield Point (YP) of API grade Bentonite, Raw Pindiga Clay and acid treated clays were determined through viscosity measurement and the results compared (Table 3).

Table 3: Rheological properties of raw and treated samples

Sample	PV (CP)	YP (lb/100ft^2)
API	4.5	6
PINDIGA	12	6
4M50	11	3
1M70	12	3
1.8M70	9	7

The clay minerals that are common exchangeable cations, are Ca^{2+}, Mg^{2+}, H^+, K^+, $NH4^+$, Na^+. However, leaching clay with acid will also affect these cations and thus, the application of the clay. The pH of clay also significantly affected its CEC (Table 4) and viscosity.[98] The CEC was determined by methylene equivalent method[13].

Table 4: CEC of raw and treated clays

S/N	Sample	Methylene Blue Capacity (meq/100 g)
1	API Grade Bentonite	44.10 ± 2.22
2	Raw Pindiga Clay	57.90 ± 1.32
3	Clay treated with *4M HCl*	34.80 ± 0.81
4	Clay treated with *1M HCl*	37.20 ± 1.50
5	Clay treated with *1.8M Oxalic acid*	38.70 0.75

Source of clays are API = MI swaco (Schlumberger), Pindiga clay = pindiga Town, NE, Nigeria

[13] Fann Instrument Company (2013) Methylene Blue Kit, Instruction Manual, Manual No. 209860, Revision E, Instrument No. 209679 & 20969 Houston, Texas, USA

4. Conclusion

Results obtained for this study using INAA and FTIR reveals that combination of high acid (4M) concentration and low temperature in Fe leaching from Pindiga clay affects the clay structure while removing less Fe and other impurities (Ti), but low acid (1M) concentration at higher temperature removes more Fe and other impurities (Ti) with less damage to the clay structure. The oxalic acid results are move close that of 1M HCl, but is removes seems to leave Ca unaffected. The results also showed that API grade Bentonite contains less Al, Fe and Ti than the Pindiga clay. However, API grade Bentonite contained more Al compounds expected in bentonite than the local clay. One of the advantages of the Pindiga clay over the API grade is that the iron content has help in improving its density to a level that barite adition might not be necessary as the case of the API grade. Therefore, what is critical in the Pindiga clays improvement to attain API standard is to improve its rheology with iron reduction.

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