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# PHYSICO-CHEMICAL PROPERTIES AND INDUSTRIAL POTENTIAL OF SOME CLAY DEPOSITS IN CALABAR AREA, SOUTH EASTERN NIGERIA

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## ABSTRACT

Clay samples collected from 10 locations in Calabar, Cross River State, Nigeria were evaluated to determine their suitability for industrial applications. The samples were pulverized, dried, sieved and quantitatively analyzed. Physical properties determined were viscosity (11-15 secs), density (1072-1769 kg $m^{-3}$), plasticity index (33-50%), particle size and firing characteristics. The clays were classified as fat clays or elastic silt. Results showed that all the clay samples were uniformly graded with fine texture and have the ideal silica value averaging 47.73% but the alumina content of the samples are lower than theoretical values of pure montmorillonite (28.3%) and kaolinite (39.5%), with averaging 18.0%. X-ray analysis indicated that the dominant clay mineral found in all the samples is kaolin with occasional illite and the main non-clay mineral as quartz. Considerable amounts of $Fe_2O_3$ (2.79-6.95%) along with some impurity oxides such as MgO (0.08-0.98%), CaO (0.12-0.95%), $K_2O$ (0.28-1.82%), $Na_2O$ (1.02-1.87%) and $TiO_2$ (0.96-1.20%) were found in all the clay minerals. These properties indicated that the clays are of low grade (non- refractory) due to the low alumina content. The low alumina content with the relatively high plasticity index and the pleasant color characteristics of the clays on firing, suggest that the clays have the potentials for use in the production of brick, ceramic and pottery products.

**KEY WORDS:** Particle Size, Silica, alumina, Kaolin, Brick, X-Ray

## INTRODUCTION

Clay minerals share a basic set of structural and chemical characteristic (they are largely aluminosilicates with layer structures) and yet each clay mineral has its own unique set of properties that determine how it will interact with other chemical species. The variation in both chemistry and structure, among the clays leads to their applications in extremely diverse fields (Costanzo, 2001). Clays are composed of certain groups of hydrous aluminum, magnesium and iron silicates that may contain sodium, calcium, potassium and other ions. These silicates collectively make up the clay minerals and the major clay mineral groups are kaolin, smectites, illites, chlorites and hormites. The specific clay minerals are identified by several techniques including thermal differential analysis (Smothens and Chang, 1966), electron microscope (Beutelspacher and Vandermarcel, 1968), infra red spectrometry (Vandermarcel and Beutelspacher, 1976) and X-ray diffraction (Brindley and Brown, 1980). Chemical analysis is an essential step to establish the nature of minerals (Newman, 1987). The chemical analysis of major elements as a baseline study of the clay minerals society source clays have been reported (Mermut *et al.,* 2001).

Generally, industrial utilization of a clay or shale deposit depends on its geological disposition, mineralogical, chemical and physical properties. The assessment of economic potentialities of clay or shale body must of

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necessity involve the evaluation of these parameters. The properties of kaolin, refractory clays, ball clays and halloysite in North America and Carribean region have been reported (Patterson and Murray, 1984) Common and important application of clays are in the manufacture of paper, paint, plastics, ink, roofing sheets, pottery, bricks, ceramics, floor tiles and rubber. Clays also find various applications in the manufacture of cement, fertilizers and insecticides (Jenson and Bateman, 1979). Hegal *et al.,* (1984) have studied the effect of composition of some Egyptian clay on their ceramic properties. The mineralogical, physical, geochemical and economic appraisal of some clay and shale deposits in southwestern and northeastern Nigeria have been discussed by Emofurieta *et al.,* (1994). The composition and industrial assessment of clay deposits in Itu, Akwa Ibom State , Southern Nigeria and South West Nigeria have been studied (Ntekim *et al.*, 1994). Okolo and Chima (1999) have reported on the physico-chemical properties of clay deposits in Bendel state, Nigeria. Based on the properties of the clay, they were found suitable for the manufacture of several industrial and household products such as paints, paper, ink, ceramic wares, roofing and floor tiles. Brick forming properties of clay deposits from Odukpani local government area of Cross River State, Nigeria from physical, mechanical and mineralogical studies have been reported (Attah *et al.*, 2001). Attah (2008), have evaluated the composition and physical properties of clay deposits in selected local government areas in Cross River state, Nigeria and found them potentially suitable for the production of refractory, pottery and building products.

Calabar and its immediate environs are located within the coastal plains sands (Benin formation) of Southern Nigeria. This is mainly a sandy formation with limes of fingers of clays (Edet *et al.,* 1994). Its temperature ranges from 21.05 to 33.15$^0$C and the annual rainfall varies from 42.0 to 1401.0 (mm/month).

This study evaluates the physical, chemical and mineralogical properties of the clay deposits in selected locations in Calabar, Nigeria to determine their industrial potentials.

## MATERIALS AND METHODS

### Sample collection

10 clay samples were collected from locations at Ambo street (AM 1, AM 2), and Anantigha (ANA) in Calabar South local government area as well as Atimbo Road (ATM), Bacoco (BAC), Export processing zone (EPZ), Ikot Effanga ( IE 1, IE 2), and Ikot Omin (IO 1, IO 2) in Calabar (Fig.1).

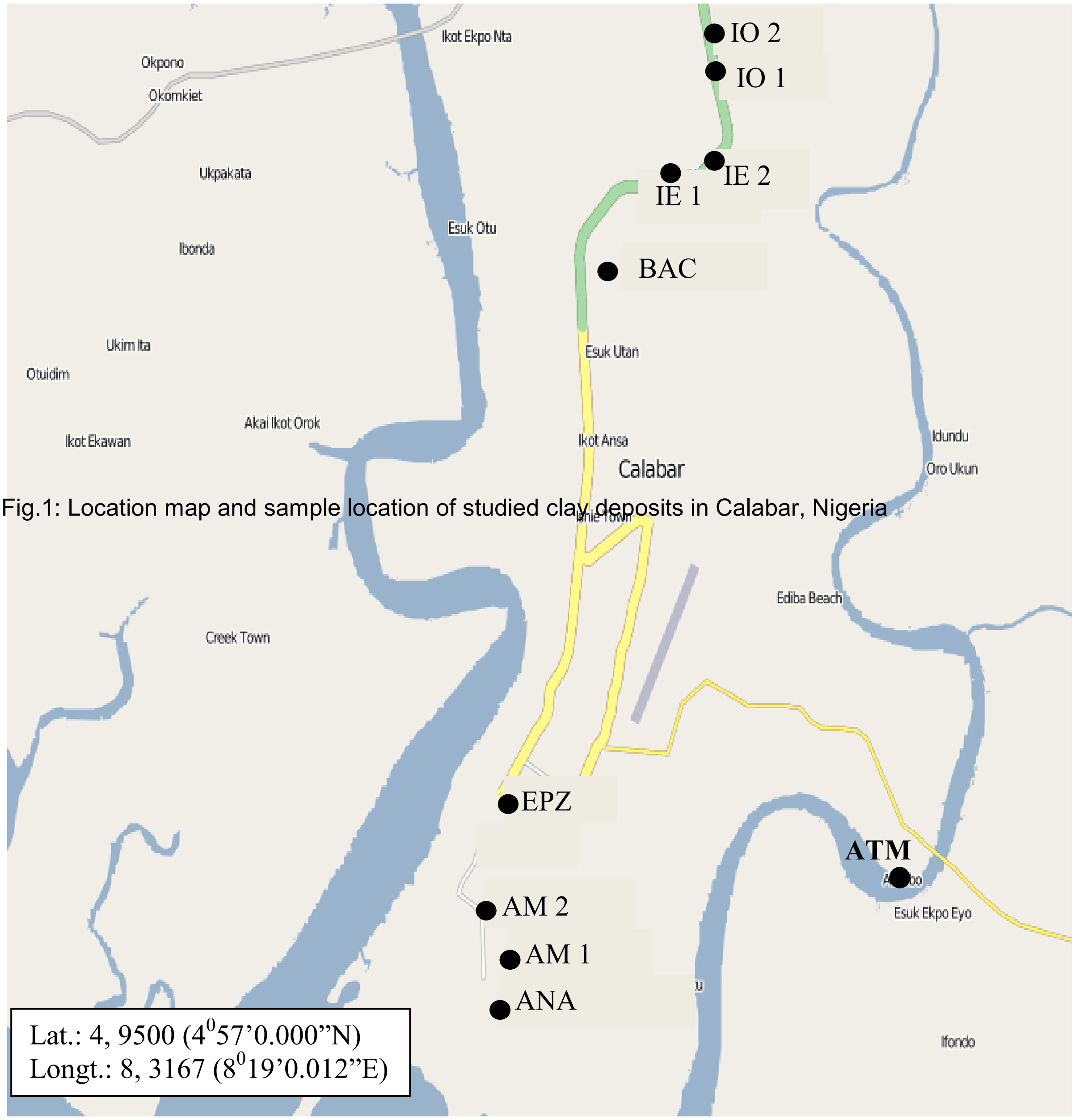


Fig.1: Location map and sample location of studied clay deposits in Calabar, Nigeria

**Laboratory analysis of clay samples**

**Reagents and Apparatus**

The chemicals used for digestion of the clay samples were $NH_4Cl$, ethanol, $AgNO_3$, hydrochloric acid (HCl), perchloric acid ($ClO_4$) and nitric acid ($HNO_3$).

Atomic Absorption Spectrophotometer (UNICAM 919) and JENWAY flame photometer were employed for chemical composition analysis.

Other apparatus used included liquid limit device, plastic limit apparatus, mechanical sieve shaker, Osworld viscometer and a Corning 240 pH meter.

### Sample preparation

In each case, 20 g of clay sample was placed in a 600 mL polyethylene centrifuge bottle and 500 mL of distilled water was added, and allowed to hydrate for 24 hrs. The suspensions were shaken thoroughly and then centrifuged for 6 min.at 600 rpm in a centrifuge. The supernatant liquid was then poured into 200 mL polypropylene cups, frozen and then placed in a freeze drier until the ice was sublimated (Constanzo,2001). The samples were placed in sealed containers before taking to the laboratory for analysis.

### Particle size and plasticity index determination

Particle size determination was carried out by soaking the samples for 24 hours and sieving with a mechanical sieve shaker using various mesh sizes of 300, 212, 150, 65 and 35μm. Plasticity index was determined using Atterberg liquid and plastic limit equipments and was calculated as the difference between liquid and plastic limits (Tan, 2005). pH was determined using Corning 240 digital pH meter while viscosity was determined using Osworld viscometer. Loss- on- ignition (LOI) tests were carried according to method of Lechler and Desiletes (1987).

### Analysis of samples

The samples were saturated with $NH_4^+$ prior to total elemental analysis following the general procedure of Brindley and Ertem (1971). The procedure involved washing the sample three times with a solution of 1M $NH_4Cl$ and then with 50% (V/V) mixture of ethanol and distilled water until the supernatant was free of $Cl^-$ by the $AgNO_3$ method. The samples were oven-dried overnight at 105°C.

The elemental composition of the clays was determined following digestion with aqua- ragia and perchloric acid. The Na, K and Ca contents were determined using Jenway Flame Emission photometer (PFP-7). All other elements, Si, Al, Fe, Mg, Mn and Ti were determined by Atomic Absorption Spectrophotometer (UNICAM 919).

Mineralogical studies were carried out using a Phillips X- ray diffractometer model PW1710. All samples were randomly mounted and analyzed serially using Cu-kα radiation at 45 kv and 20 mA.at the scan speed of $2^0$ per minute.

## STATISTICAL ANALYSIS

Values for the Si, Al, Fe and Ti oxides were reported as the mean of five determinations (n=5) ± standard deviation (SD).

## RESULTS AND DISCUSSION

The location map and sample location sites of the clay deposits are shown in Fig.1. From the results of particle size distributions shown in Fig.2, the clay samples are uniformly graded. Judging from the high percentages passing through the 35μm sieve size, these clays are quite fine in size. By this criterion, ATM clay which was the finest has over 88% passing, while EPZ clay, the coarsest has 75% passing through the 35μm mesh.

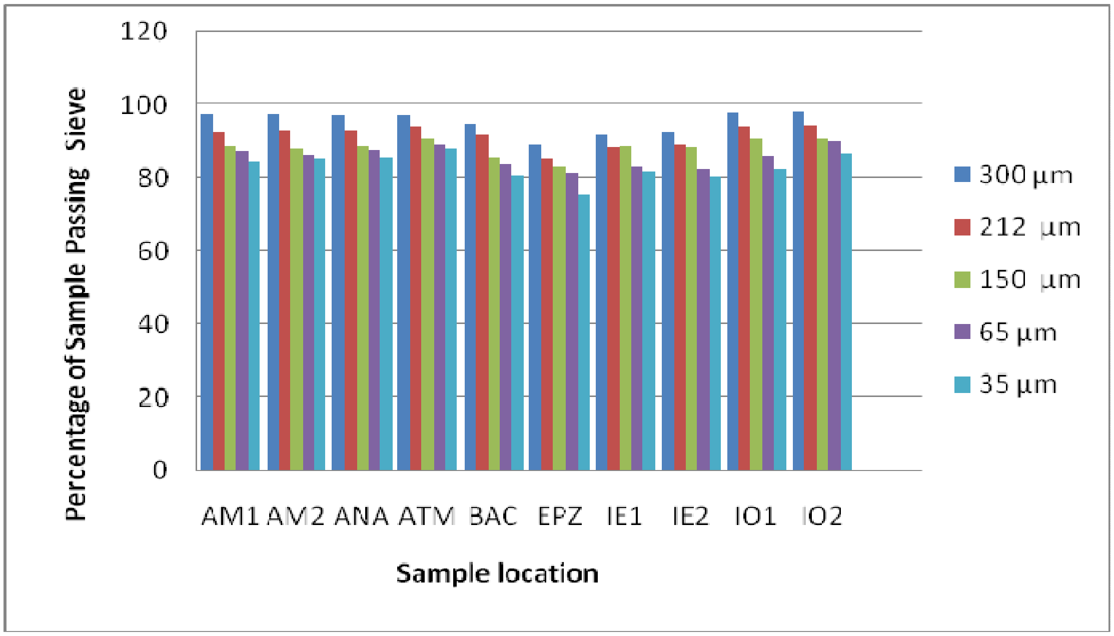


**Fig. 2 Particle size analysis of clay mineral samples**

Table 1 shows the results of density, viscosity and plasticity index for the clay samples. Density values ranged from 1436 to 1769 kg $m^{-3}$ for AM 1 and 2, BAC and EPZ clays while others have density values ranging from 1073 to 1334 kg $m^{-3}$. The densities of clays and indeed other earth materials tend to be inversely proportional to the moisture content (Grim, 1968). Viscosity values for the clay samples which ranged from 11 to 15 secs. suggest that they can be prepared into slips for casting easily. Viscosity values of the clays used for drain-cast slips are generally much lower than those for solid- cast slips (Norton, 1974). The clays have medium to high plasticity index values (33-50%). The high plasticity can be attributed to the general fineness of the particles and on the plasticity chart as shown in Fig.3, clay samples from IE 2 and IO 2 which are below the A-line are projected as inorganic silts of high compressibility while all other samples which are above or on the A-line are projected as inorganic clays with high compressibility (Cassagrande, 1932a). X-ray diffractograms of the clay minerals show similar composition (Moore and Reynolds, 1997). Fig. 4 shows the X-ray diffractogram for IE 1 clay. The dominant clay mineral found was kaolin with occasional illite and the main non-clay mineral was quartz.

**Table 1: Physical properties and classification of the clay minerals**

| Sample Location | Viscosity (secs) | Density (Kg m$^{-3}$) | Liquid Limit (%) | Plastic Limit (%) | Plasticity Index (%) | *Classification |
|---|---|---|---|---|---|---|
| **AM 1** | 12 | 1436 | 75 | 29 | 46 | CH |
| **AM 2** | 11 | 1571 | 75 | 29 | 46 | CH |
| **ANA** | 14 | 1324 | 78 | 29 | 49 | CH |
| **ATM** | 12 | 1280 | 79 | 36 | 43 | CH |
| **BAC** | 13 | 1769 | 73 | 25 | 48 | CH |
| **EPZ** | 13 | 1755 | 82 | 38 | 44 | CH |
| **IE 1** | 14 | 1197 | 61 | 25 | 36 | CH |
| **IE 2** | 14 | 1072 | 83 | 50 | 33 | MH |
| **IO 1** | 14 | 1233 | 75 | 25 | 50 | CH |
| **IO 2** | 15 | 1334 | 90 | 50 | 40 | MH |

***CH:** Clay of high plasticity, Fat clay
**MH:** Silt of high plasticity, Elastic silt

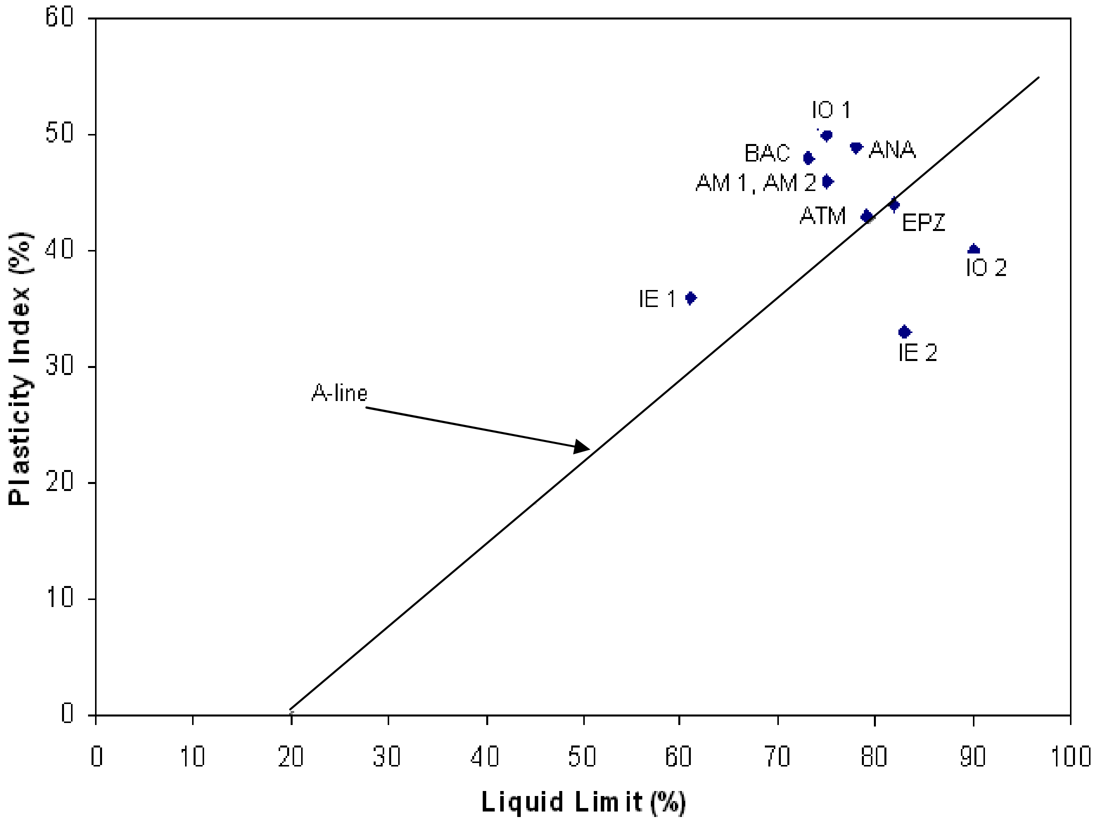
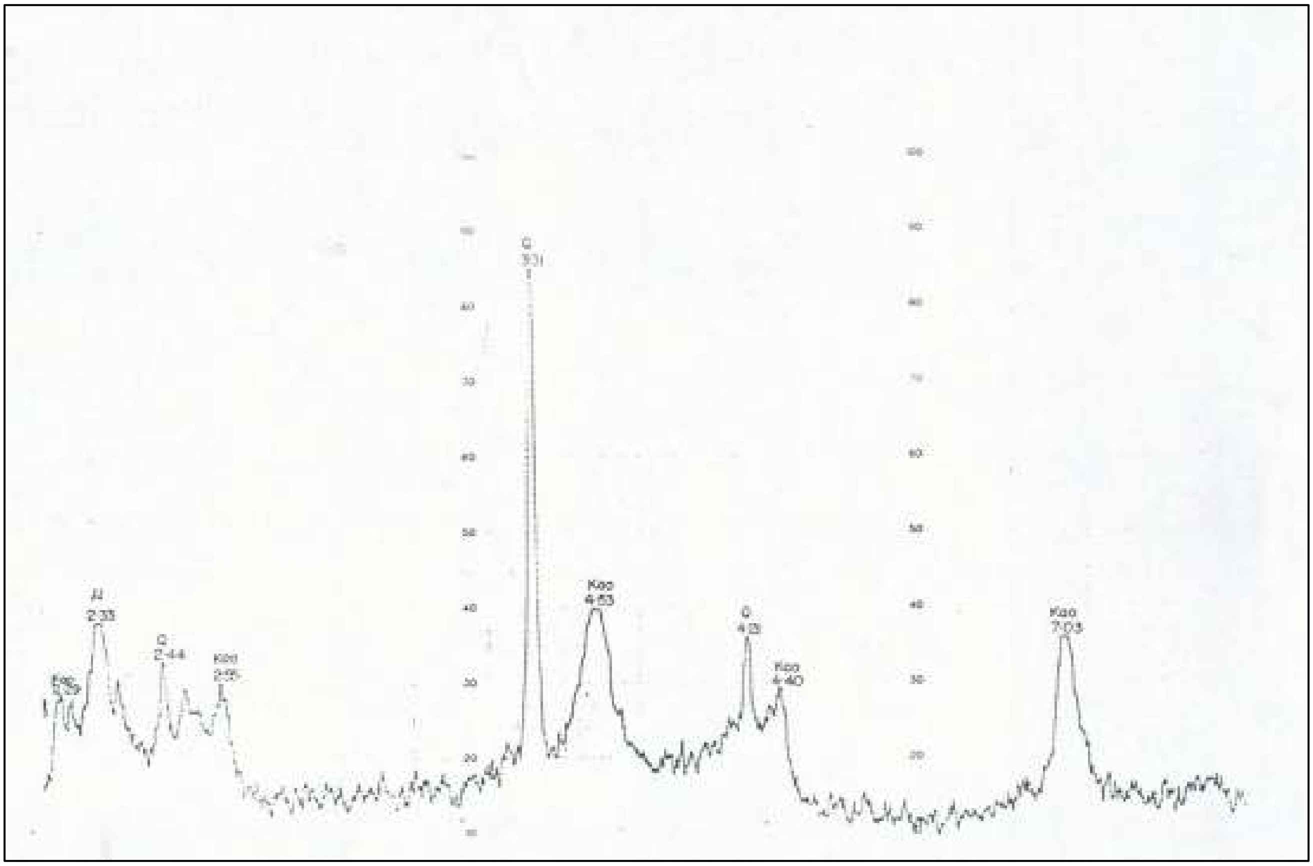


Fig.3: Plasticity chart of clay minerals



The chemical composition of the clay samples are presented in Table 2. The pH values (3.10-5.09) reveal that the clays are more of acidic variety coming from tertiary - to-recent environment. All the samples have the ideal silica value averaging 47.73% but the alumina content of the samples are lower than theoretical values of pure montmorillonite (28.3%) and kaolinite (39.5%) (Murray, 1960), averaging 18.0% which compared with Egyptian El-Melouk clay found suitable for production of ceramic wares (Hegab *et al*, 1984). Considerable amounts of Fe and Ti were found respectively in BAC (6.95 and 1.01%), IE 2 (6.630 and 1.4%) clays, which suggested the presence of impurities in the two samples. Many kaolinites contain titanites together with Fe-rich oxides as impurities especially those found in soils under tropical conditions. Other impurity oxides found were CaO (0.12-0.95%), MgO (0.08-0.98%), $K_2O$ (0.28-1.82%) and $Na_2O$ (1.02-1.82%). Although the Ca and Mg contents are quite low in all the samples, K and Na contents are higher in IE 1 clay with the lowest K and Mg contents found in the EPZ and BAC clay samples. The presence of K in the samples can be attributed to K-bearing minerals (Mermut *et al*, 2001).

**Table 2: pH and chemical composition of the clay minerals (%)**

| Sample location | pH | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | MgO | $K_2O$ | $Na_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| **AM 1** | 3.32 | 48.13 ± 0.09 | 18.10 ±0.08 | 3.65 ± 0.03 | 1.02 ± 0.06 | 0.23 | 0.23 | 1.05 | 1.19 |
| **AM 2** | 4.20 | 48.13 ± 0.02 | 17.06 ± 0.03 | 3.65 ± 0.04 | 1.04 ± 0.08 | 0.95 | 0.98 | 0.98 | 1.07 |
| **ANA** | 3.10 | 46.79 ± 0.12 | 18.19 ± 0.08 | 4.30 ± 0.11 | 0.98 ± 0.01 | 0.15 | 0.11 | 0.75 | 1.07 |
| **ATM** | 4.15 | 46.97 ± 0.19 | 17.96 ± 0.04 | 5.40 ± 0.06 | 0.98 ± 0.08 | 0.15 | 0.15 | 0.50 | 1.47 |
| **BAC** | 4.80 | 48.13 ± 0.14 | 17.96 ± 0.05 | 6.95 ± 0.04 | 1.01 ± 0.05 | 0.58 | 0.08 | 0.43 | 1.62 |
| **EPZ** | 4.35 | 46.79 ± 0.19 | 17.96 ± 0.05 | 4.30 ± 0.04 | 1.06 ± 0.05 | 0.37 | 0.29 | 0.28 | 1.09 |
| **IE1** | 3.67 | 49.46 ± 0.16 | 18.00 ± 0.03 | 2.79 ± 0.04 | 1.20 ± 0.05 | 0.12 | 0.98 | 1.82 | 1.82 |
| **IE 2** | 4.37 | 49.46 ± 0.28 | 18.00 ± 0.08 | 6.63 ± 0.06 | 1.40 ± 0.08 | 0.20 | 0.18 | 0.56 | 1.67 |
| **IO 1** | 4.80 | 46.79 ± 0.14 | 16.77 ± 0.07 | 3.98 ± 0.04 | 1.00 ± 0.06 | 0.18 | 0.16 | 0.75 | 1.08 |
| **IO 2** | 5.09 | 46.79 ± 0.15 | 17.25 ± 0.05 | 4.25 ± 0.02 | 0.96 ± 0.06 | 0.31 | 0.25 | 0.60 | 1.07 |

Table 3 shows the result of total oxides and firing characteristics of the clay minerals. The loss-on-ignition (LOI), which is the amount of shrinkage, increased as the firing temperature increased from 110°C to 1200°C in all the clay samples reaching a maximum of 19.36% for the IO 1 sample.

**Table 3: Total oxides and firing characteristics of the clay minerals**

| Sample | Total oxides ( %) | LOI (%) 110-550°C | LOI (%) 550-1200°C | Total (%) | Color change |
|---|---|---|---|---|---|
| **AM 1** | 73.60 | 7.80 | 18.00 | 99.40 | Grey to ash grey |
| **AM 2** | 73.86 | 7.80 | 18.02 | 99.68 | Grey to ash grey |
| **ANA** | 72.34 | 7.88 | 18.72 | 99.46 | Grey to mild grey |
| **ATM** | 73.58 | 7.47 | 18.50 | 99.31 | Light brown |
| **BAC** | 76.76 | 5.30 | 17.10 | 99.16 | Light brown |
| **EPZ** | 72.14 | 8.16 | 18.90 | 99.20 | Black to mild grey |
| **IE 1** | 76.19 | 5.36 | 17.67 | 99.22 | Black to mild grey |
| **IE 2** | 78.10 | 4.88 | 16.95 | 99.93 | Pale pink |
| **IO 1** | 70.71 | 9.16 | 19.36 | 99.23 | Pale pink |
| **IO 2** | 71.48 | 9.16 | 19.16 | 99.80 | Pale pink |

**LOI: Loss-on -ignition**

The firing color of the clays varied from grey to ash grey for AM 1, AM 2 and ANA samples, light brown for ATM and BAC samples, black to mild grey for EPZ and IE 1 and pale pink for IE 2, IO 1 and IO 2 samples. The higher concentrations of iron and titanium oxides however gave rise to the brownish and pinkish firing colors observed for ATM, BAC, IE 2, IO 1 and IO 2 clay samples respectively, thereby rendering them unsuitable for the paper industry (Nurse,1960). They are however suitable for brick, cement, ceramic and pottery production and can also be refined to reduce the iron and titanium oxides to the desired level for paper production although the process may be expensive for industrial purposes (Akpokodje *et al*, 1991). From the ceramic point of view (Clews, 1955; Norton, 1974; Worral, 1976; Attah *et al*, 2001; Attah, 2008), the investigated clays can be considered as low-grade clays due to the considerable amount of $Fe_2O_3$ and other impurity oxides and therefore suitable for the manufacture of heavy clay products such as building bricks, ceramic tiles and pottery products.

## CONCLUSION

All the clay samples investigated are of uniform grade and judging from the high percentage (>80%) passing through the 35μm sieve size, these clays are quite fine in size. From the pleasant color characteristics on firing, the high plasticity index and the low alumina content, these clays are suitable for the manufacture of bricks, ceramic tiles and pottery products (Akpokodje *et al*, 1991; Attah *et al*, 2001; Attah, 2008).

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