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Mineralogical and Chemical Evaluation of Agbaja Fireclay for Industrial Applications

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Abstract

To evaluate the potential of Agbaja clay for industrial applications, a comprehensive analysis of its physico-chemical and mineralogical properties was undertaken. The clay exhibited a predominantly kaolinitic composition, as determined by X-ray powder diffraction (XRD), with halloysite and illite as minor constituents. The chemical analysis revealed significant alumina (Al_2O_3) and silica (SiO_2) content at 38.68 wt% and 39.47 wt%, respectively, along with negligible alkali oxide impurities. The clay demonstrated plastic behavior with an Atterberg Plasticity Index of 15.45% and a neutral pH of 6.61. Based on these findings, Agbaja clay is deemed suitable for a wide range of applications including the production of refractory materials, vitreous ceramics, and as a filler in paper, rubber, plastic, and pharmaceutical industries. A notable characteristic is the colour transformation from milk white to light grey upon firing.

Keywords: Agbaja Clay, Atterberg Plasticity Index, X-ray fluorescence, X-ray diffraction

1.0. INTRODUCTION

Clays constitute a diverse group of mineral commodities characterized by distinct mineralogy, geological formation, extraction techniques, and end-use applications (Dumont, 2003). Broadly categorized into specialty clays, encompassing bentonite, fuller's earth, and montmorillonite, and kaolin clays, including ball clay, fireclay (refractory clay), stoneware, and kaolin, these materials seldom exist in pure form. Instead, they are typically associated with gangue minerals such as quartz, calcite, dolomite, feldspar, gypsum, and iron oxides, whose presence may or may not adversely impact their suitability for ceramic applications.

The commercial value of clay depends primarily on its physical properties such as plasticity, strength, shrinkage, vitrification range, refractoriness, fired colour, porosity and absorption. The wide application of clay in homes and industries is based on its intrinsic properties such as high chemical durability, high aesthetic value, wear resistance, high strength at elevated temperatures and thermal resistance (Nnuka *et al.,* 1992). Thus, clays are versatile industrial raw materials needed for the manufacture of domestic and industrial products such as pottery and ceramic wares, bricks, electrical insulators, paper, print ink, roofing and floor tiles. Clays also find various applications in the manufacture of cement, plastics, fertilizers and insecticides (Nnuka *et al.,* 2001).

To sustain the development, manufacture and growth of ceramic and allied industries in Nigeria, raw materials analysis, development and processing are most relevant (Onaji *et al.,* 1995 and Irabor, 2002). Oaikhinan, (1999) estimated that well over 300,000 metric ton of processed clay are required in Nigeria, annually, while the current consumption is met from poor local production of about 50,000 metric ton per annum and foreign import accounts for the remaining annual supply of over 250,000 metric ton. The trust of this paper is to investigate Agbaja clay in order to ascertain its suitability for ceramic production and other industrial applications.

2.0. MATERIALS AND METHODS

The raw clay samples were collected from Agbaja village situated on a plateau in Lokoja Local Government Area of Kogi State. The samples were collected in lumps at depths of between 3-5 meters at different locations on the plateau. The lumps were crushed into powder and mixed thoroughly to obtain a homogeneous representative sample. About three-quarters of the representative sample were beneficiated by washing. The washed clay was dried under ambient condition on a cemented floor and then pulverized. The raw and beneficiated samples were then characterized for particle size distribution, plasticity index, chemical composition and mineralogy.

2.1. Natural water content

The natural water content was determined by the procedure used by Nnuka *et al.,* (2001). The sample was crushed to pass through a 1mm sieve. It was then thoroughly mixed by rolling and weighed before heating in an electric oven at 115°C for 5.5 hours. The heated sample is cooled in a desiccator overnight. The sample is then weighed to note the weight lost. The weighing is repeated on a daily basis until a constant weight is obtained. The natural water content (Wn) was calculated using Equation 1.

$$Wn = \frac{Mass\ of\ water}{Mass\ of\ oven\ dried\ sample}\ x\ 10 \ldots\ldots (1)$$

2.2 Loss of Ignition (L.O.I)

1gm of the sample was weighed into a porcelain crucible. The crucible was then placed in a muffle furnace and the temperature was gradually increased from 320ºC to 1000ºC and maintained for 2 hours. The crucible was removed, allowed to cool further in a desiccator and weighed. The crucible was returned into the furnace for about 10 minutes and reweighed. This was continued until a constant weight was obtained. The L.O.I. was calculated using the formula in equation1.

$$LOI = \frac{M - m}{M} x\ 100 \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where: M = mass of sample (g)
m = mass of sample after igniton (g)

2.3. pH determination

The method used for the pH analysis is as described by Ekosse *et al.,* (2000). 2.5g aliquots of finely ground clay samples were placed in 3 centrifuge tubes and suspended in 25ml of distilled water. After shaking on a horizontal shaker for about 30 minutes, the tubes were then centrifuged for 5 minutes and the pH of the supernatant was determined using an ELE International 3071 pH meter. Average values were calculated from three readings and recorded for the sample analyzed.

2.4. Plasticity

Atterberg plasticity test was performed by determining the liquid limit (LL) and the plastic limit (PL) of the clay. The plasticity index (PI) was evaluated as the arithmetic difference between the LL and the PL values. The LL and PL values were determined using the cassagrande equipment at the National Steel Council, Kaduna as described by Casagrande (1948), Grim (1962) and Ekosse *et al.,* (2000).

2.5. Sedimentological Analysis

The grain size distribution of the sample clay from Agbaja clay deposit was determined using the hydrometer method (Krynine and Judd, 1957) based on the stoke's law which states, that particles of different sizes have different settling velocities. 50g of air-dried clay sample was ground and sieved through Tyler mesh sieve No. 200 (i.e. 0.075mm) for this analysis which was carried out at National Steel Council, Kaduna.

2.6. Soil Activity (A)

The soil activity for the clay was calculated according to equation 3.

$$A = \frac{PI}{\%Clay} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where: PI = plasticity index and %clay = percentage clay passing.

2.7. Chemical Analysis (XRF)

The X-ray fluorescence analysis was carried out at the National Geo-science Research Laboratory in Kaduna. The samples to be analyzed were ground into a powder in an agate mortar to particle sizes less than 125µm. Pellets each of diameter size of 19mm were prepared from 0.5g of the powder by mixing the powder with three drops of organic liquid binder (epoxy glue) and pressing with hydraulic press to 10 tones.

Each pellet was placed on a holder in the specimen chamber. Radiation emerging from the X-ray tube window excites secondary X-ray Spectra of elements within the pellet. These secondary X-ray emissions which were characteristic of the elements being analyzed were intercepted by the detector and transformed into voltage signals for processing.

2.8. Mineralogical Analysis (XRD).

The X-ray diffraction analysis was conducted at the laboratory of the National Steel Raw Material Council, Kaduna to determine their mineral phase constituents. For this determination, untreated clay samples were pulverized while the fine clay fractions of < 2µm were prepared based on the principle of sedimentation. The powdered samples were each mixed with a few drops of epoxy glue to minimize their preferred orientation and allowed to dry in an oven. The dried samples were gently crushed in an agate mortar to a fine texture. The powder samples were mounted (with very little pressure, using a blade to minimize preferred orientation of the kaolinite particles) on the sample holder of the computer-controlled diffractometer, type PX1800, with an automatic divergence slit, and a Cu anode producing X-rays of wavelengths λ1 = 1.54056 Å and λ2 = 1.54439 Å. The diffractometer operated at 40kv and 55mA and the automatic routines allowed scanning for values of 2Θ from 5º to 70º, using a step size of 0.02º and time per step of 0.30 S.

From the XRD traces, clay minerals were determined by their diagnostic peaks and conversion of 2θ to dÅ was made using the mineral table of conversion.

3.0. RESULTS AND DISCUSSION

3.1. Natural water content

The natural water content of Agbaja clay, determined to be 7.56 wt% (Table 1), falls within the moderate range. However, this value suggests a relatively low water retention capacity for the clay. The limited water holding ability may be attributed to the low organic matter content, as organic matter is known to enhance soil moisture retention (Brady and Weil, 2002). The pH of 6.16 indicates a slightly alkaline condition and a low concentration of soluble salts, aligning with Murray's (1986) observation that clays with pH values exceeding 6.5 typically exhibit higher soluble salt content.

3.2. Plasticity

The intersection of the plasticity index (15.45%) and the liquid limit (40.45%) above the "A" line separating the inorganic clays from inorganic silts on the Casagrande plasticity index chart (Figure.1.) classifies Agbaja clay as inorganic clay of intermediate plasticity according to the Unified Soil Classification System (USCS). With a soil activity value (swelling potential) of about 34.33wt%, Agbaja clay can be appropriately described to have a fairly low water retention capacity. This characteristic could be attributed to the low organic matter content and the dominance of the kaolinite mineral in the clay.

3.3. Sedimentological Analysis.

The particle size distribution for the raw clay samples (Figures 2.) indicates a clay percentage passing of 45%, a silt range of 12% and a predominantly coarse range. The dominance of the coarse range could be attributed to a defect in the sample preparation. The high percentage clay passing of 100%wt% of particle size <2µm for the beneficiated clay sample as indicated in the sedigraph (Figure.3.) is an indication of the ease with which the silt range can be eliminated fo this clay sample. This makes Agbaja clay very useful for polymer extension and reinforcement in the plastic, rubber and paper industries where surface chemistry and particle size are of primary importance. The finer the particle size, the finer the reinforcement (Bundy, 1993 and Ekosse, 1994). The high percentage fine of the sample implies that the clay must have been of a secondary origin formed from weathering of exposed basement feldspathic and volcanic rocks and transported to its present site by erosion.

3.4. Chemical Analysis (XRF)

The chemical composition and loss of ignition for the unbeneficiated and beneficiated clay samples are shown in Table 2. The dominant oxides for both the untreated and treated samples are Al_20_3 and $Si0_2$. They have a combined oxide composition of 78.15wt%. The loss on ignition of 12.53wt % is associated with the presence of clay minerals, hydroxides and organic matter. The average values for calcia 0.38wt%, potash 0.23wt% and iron 0.68wt% contents are all within tolerable impurity range for kaolinite, brick clay, ceramics and refractory applications (Grimshaw, 1971, Murray, 1960, Singer and Singer, 1963 and Parker, 1967).

The combined average alkali oxide content of 0.61wt% must have imparted the medium plasticity property on the clay. The 0.68wt% Fe_20_3 content is an indication of an oxidizing environment (Weaver, 1989). This must have resulted in the mild change in the clay colour from milk white to light grey upon sintering at 1200°C.

The combined value of Al_20_3 and $Si0_2$ of about 78.15wt% coupled with the low alkali content of 0.61wt% makes the clay suitable for the production of firebricks (Adekanmbi 2005) and super-heat duty fireclay refractory material (Chesti, 1994).

Table 1. Physical Characteristics of Agbaja Clay

Plasticity	Unbeneficiated	Beneficiated	Natural Water Content ai 115°C (wt%)	Soil Activity (A) (%)	Firing Characteristics	
Liquid Limit	41.90	39.00	7.3	34.33	Temp. °C	colour Change
Plastic Limit	26.00	25.10			115°C	Milk White
Atterberg Plasticity Index	15.90	15.00			1200°C	Light Grey

Table 2. Chemical Composition of Agbaja Clay in Comparison with Ranges for Industrial Applications

Oxides	**Agbaja Clay**		**Ceramics***	**Refractories+**	**Brick Clay#**	**Kaolin$**
	Untreated	**Treated**				
Al_2O_3 (wt%)	38.19	39.16	26.5	25–44	9 – 45	25– 45
SiO_2 (wt%)	39.99	38.93	67.5	51-70	38 – 67	40-60
Fe_2O_3 (wt%)	0.68	0.67	0.5-1.2	0.5-2.4	2 – 7	1–5
K_2O (wt%)	0.23	0.22	0.10–3.1	-	2 – 7	-
CaO (wt%)	0.39	0.37	0.18-0.3	0.1-0.2	1 – 5	<2.5
MgO (wt%)	ND	ND	0.1-0.19	0.2–0.7	0.5 – 0.8	-
Na_2O (wt%)	ND	ND	0.20-1.5	0.8-3.5	2.7 – 6.0	-
LOI (wt%)	13.01	12.05	4 – 51	-	13 – 40	5-14

Sources: *Singer and Singer (1963), +Parker (1967), #Murray (1960) and $Grimshaw (1971).

3.5. Mineralogical composition

X-ray diffraction (XRD) analysis of both the beneficiated and unbeneficiated bulk clay samples (Figures 4 and 5) revealed a predominant kaolinite mineralogy. The characteristic diffraction peaks at approximately 2.5° 2θ (d = 7.1 Å) and 24.9° 2θ (d = 3.5 Å) are diagnostic of the kaolinite structure (Moore and Reynolds, 1997). The presence of additional basal reflections in the XRD patterns indicates the co-existence of other clay minerals, namely halloysite and illite. These minerals are commonly associated with kaolinite in sedimentary environments due to their similar geochemical conditions of formation (Grim, 1968). The identification of these clay minerals is crucial for understanding the physicochemical properties and potential applications of the clay material.

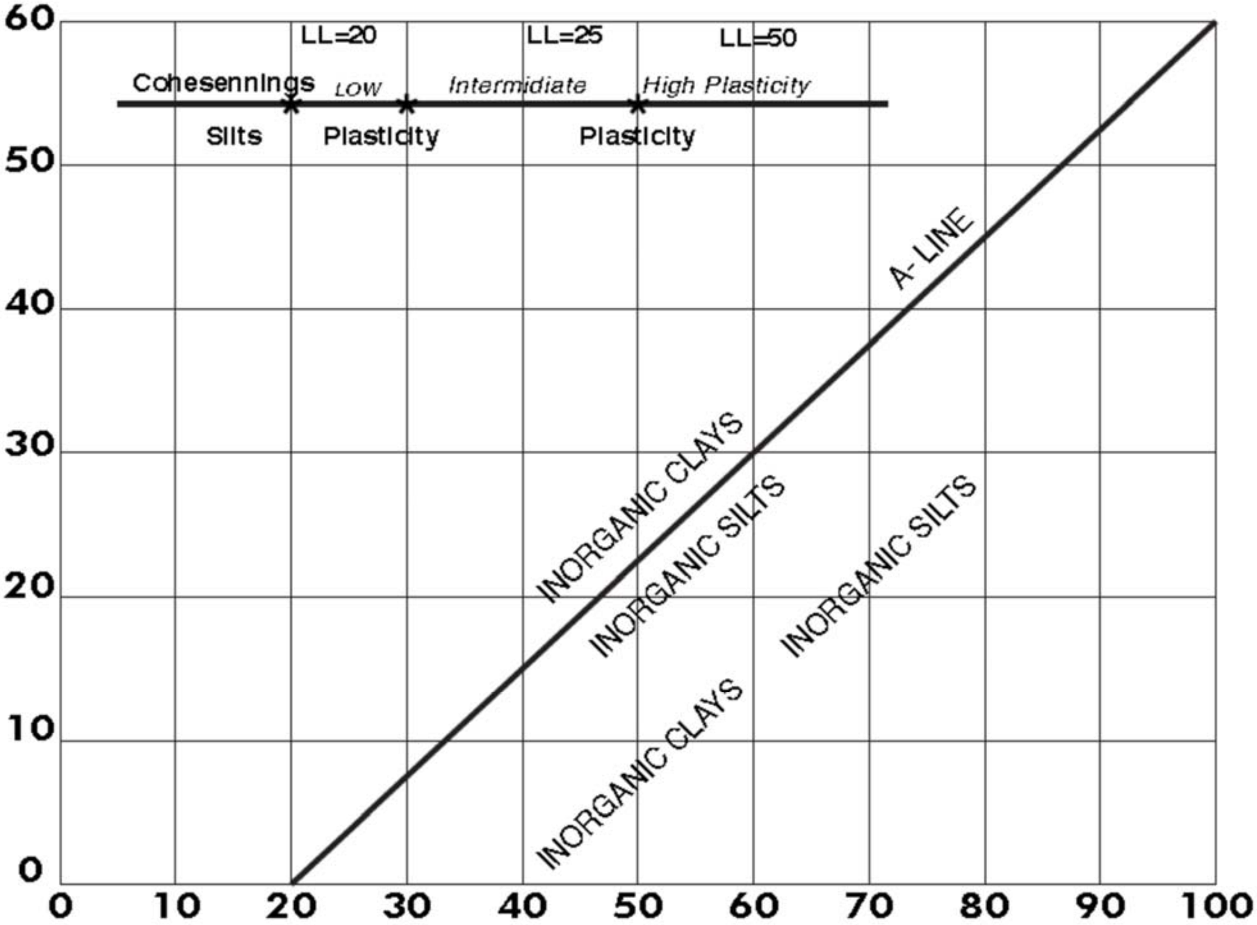

Figure 1: Casagrande Plasticity Chart for Agbaja Clay

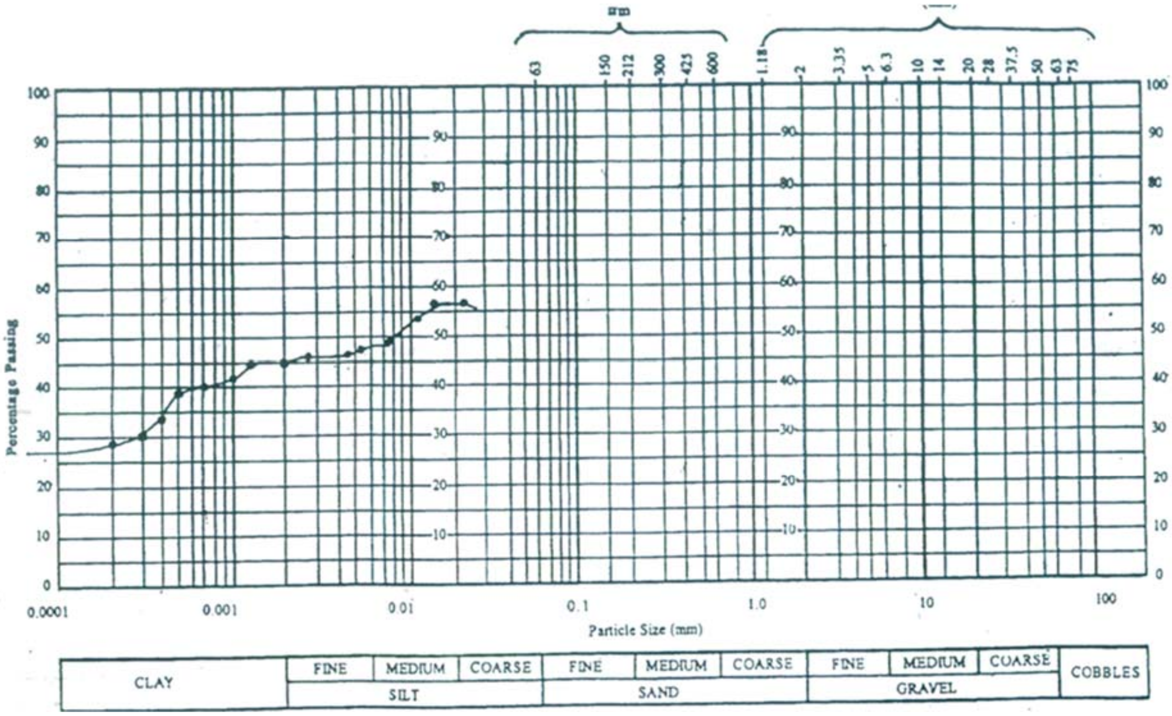

Figure 2. SEDIGRAPH for Unbeneficiated Agbaja Clay Sample

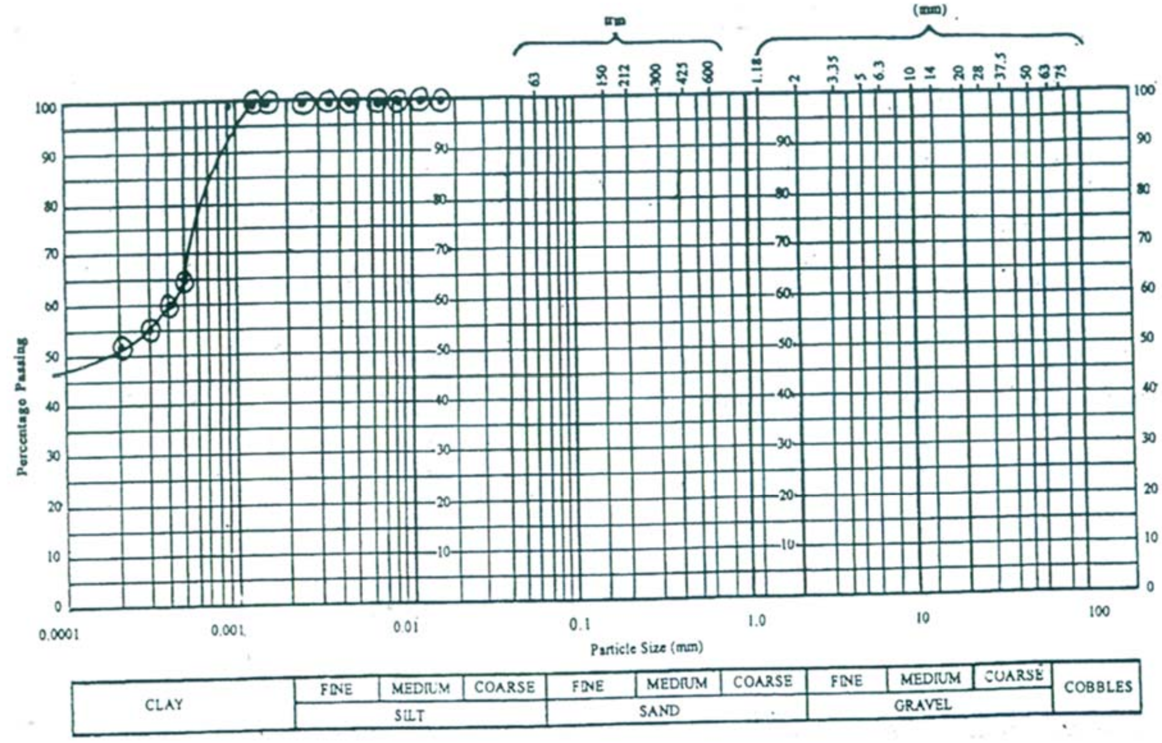

Figure 3. SEDIGRAPH for Beneficiated Agbaja Clay Sample

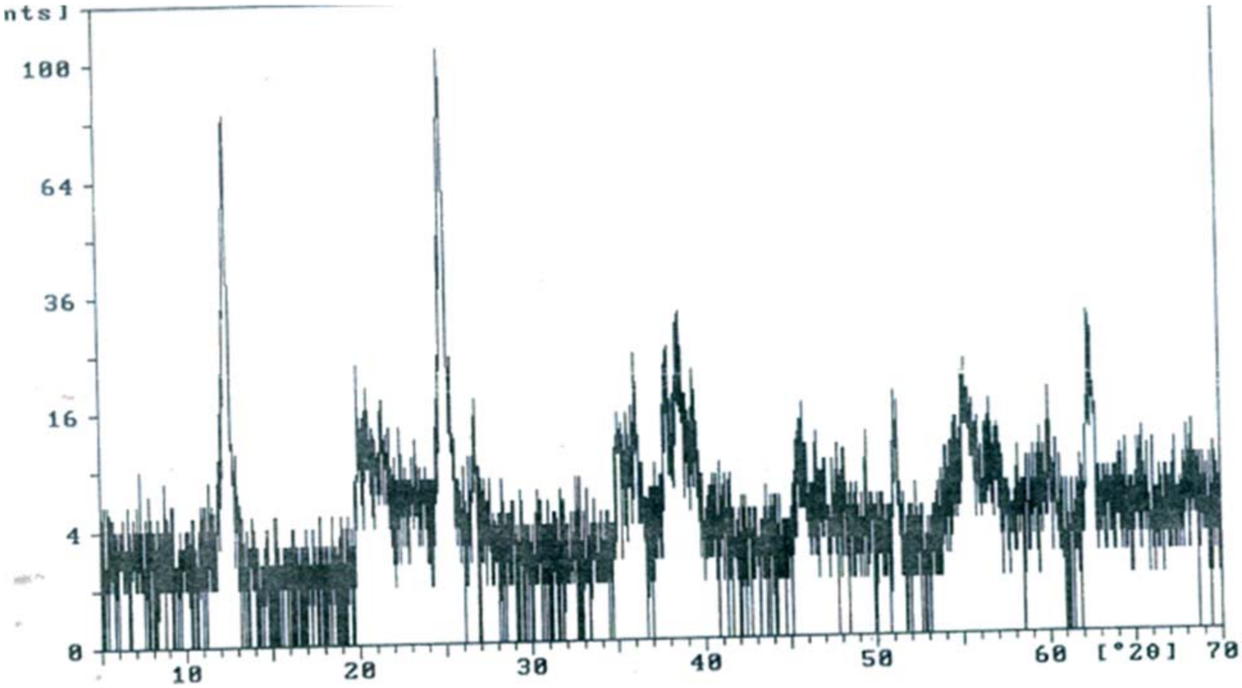

Figure 4. XRD Diffractogram for Bulk Unbeneficiated Agbaja Clay

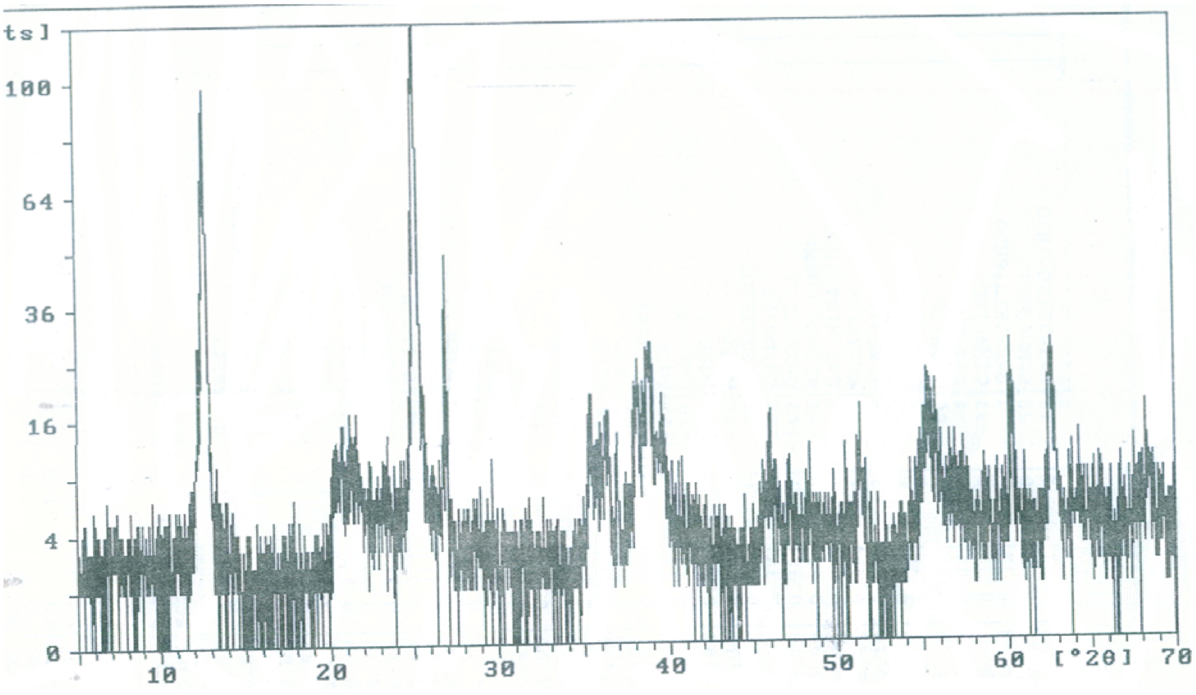

Figure 5. XRD Diffractogram for Beneficiated Agbaja Clay

4.0. CONCLUSIONS

Physico-chemical analyses on Agbaja clay revealed that the clay was in the fireclay class. The low alkali oxide content of 0.61wt% must have helped impart the intermediate plasticity properties on the clay. The low Atterberg plasticity Index value of 15.45wt% and the soil activity value of 34.33wt% is an indication of a low water retention capacity which ensures a low shrinkage level. Thus, the clay can be said to be quite suitable for the production of ceramic and refractory materials. The 100% clay particle passing value for the beneficiated clay is an indication of the economic viability in its processing, thus making the clay very useful for polymer extension and reinforcement in the rubber, plastic and paper industries. The XRD results confirmed that the clay contained predominantly kaolinites, while the light grey colouration on firing was indicative of the presence of only a small amount ferrogenious mineral. Other minerals present in the clay were halloysite and illite.

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