Chemsearch Journal 3(2): 53 – 60, December, 2012
Publication of Chemical Society of Nigeria, Kano Chapter
Date Received: November, 2012
Date Accepted: December, 2012
ISSN: 2276 – 707X

A STUDY OF THE PHYSICO-CHEMISTRY AND MINERALOGY OF AGBAJA CLAY FOR ITS INDUSTRIAL APPLICATION.

Abdullahi, Y.; Ali, E.A. and Oyeyemi, S.*
Department of Industrial Design (Glass Technology) Ahmadu Bello University, Zaria
*Department of Applied Science, Kaduna Polytechnic, kaduna
Email: egeneja66@yahoo.com

ABSTRACT

Agbaja clay was analyzed for its physico-chemical and x-ray properties to ascertain its suitability for ceramic, refractory and other industrial applications. The clay was found to be predominantly composed of Al_2O_3 (38.68%), SiO_2 (39.47%) alkali oxides (0.61%). It had a pH value of 6.61, an Atterberg Plasticity Index of 15.45%. X – ray powder diffraction (XRD) analysis showed kaolinite as the main mineral phase while Halloysite and Illite were the accessory minerals present. Agbaja clay is suitable for use in the production of super-heat duty refractory materials and vitreous ceramic wares. It is also suitable for use in the paper, rubber, plastic and pharmaceutical industries. The clay color changed from milk white to light grey upon firing.

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

INTRODUCTION

Clays are a complex group that consists of several mineral commodities, each having different mineralogy, geological occurrence, mining /processing technology and uses (Dumont, 2003). Clays are classified into two broad groups namely specialty clays which include bentonite, fullers earth and montmorrilonite and kaolinte clays which include ball clay, fire clay (refractory clay), stone ware and kaolinte. These minerals rarely occur in a pure state and occur with gangue minerals (e.g. quartz, calcite, dolomite, feldspar, gypsum and iron oxide), which may or may not be deleterious for ceramic applications.

The commercial value of clay depends primarily on its physical properties such as plasticity, strength, shrinkage, vitrification range, refractoriness, fired color, 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 (NnukaandEnejor2001).

To sustain the development, manufacture and growth of ceramic and allied industries in Nigeria, raw materials analysis, development and processing are most relevant (Onajiand Ahmed 1995;Irabor, 2002).

Oaikhinan, (1999) estimated that well over 300,000 metric tons 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 tons.

The aim of the study reported in this paper is to investigate Agbaja clay in order to ascertain its suitability for ceramic production and other industrial applications.

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.

Natural water content.

The natural water content was determined by the procedure used by Nnuka and Enejor, (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 ½ hours. The heated sample is cooled in a desiccator overnight. The sample is then weighed to note the weight lost. The weighing was repeated on a daily basis until a constant weight was obtained. The natural water content (Wn) was calculated using Equation 1.

$$Wn = \frac{Mass\ of\ oven\ dry\ sample}{Mass\ of\ sample\ before\ oven\ drying}\ x\ 100 \ldots\ldots\ldots\ldots\ldots (1)$$

Loss of Ignition (L.O.I)

The sample (1g) was weighed into a porcelain crucible. The crucible was then placed in a muffle furnace and the temperature was gradually increased from 320°C to 1000°C and maintained for 2 hours. The crucible was removed, allowed to cool 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.

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

Where: M = mass of sample (g)
m = mass of sample after ignition (g)

pH determination.

The method used for the pH analysis is as described by Ekosseand Nkoma(2000). Aliquots (2.5g) 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 value was calculated from three readings and recorded.

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 Ekosseand Nkoma(2000).

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 thestoke's law which states, that particles of different sizes have different settling velocities. A air-dried clay sample (50g) was ground and sieved through Tyler mesh sieve No. 200 (i.e. 0.075mm) for this analysis which was carried out at National Steel Raw Material Council, Kaduna.

Soil Activity (A)

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

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

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

X-ray FluorescenceAnalysis (XRF)

The X-ray fluorescence analysis was carried out at the National Geo-science Research Laboratory in Kaduna. The samples were analyzed using XRFMini Pal 4Machine (PW 4030 X-ray Spectrometer), which is an energy dispersive microprocessor controlled analytical instrument designed for the detection and measurement of elements in solids, powders or liquids. The samples were ground into a powder in an agate mortar to particle sizes less than 125µm. Pellets of 19mm size in diameter 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.

Mineralogical Analysis (XRD).

The X-ray diffraction analysis was conducted at the laboratory of the National Steel Raw Material Council in 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 5^o to 70^o, using a step size of 0.02^o and time per step of 0.30 s.

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

RESULTS AND DISCUSSION

Natural water content

The natural water content value of 7.26% (Table 1.) can be described as moderate. This observed value indicate that the water retention capacity of Agbaja clay is low, which may be attributed to the presence of low organic matter content. The pH value of 6.16 indicates a low level of soluble salt content in the clay. According to Murray, (1986), clay with pH value of > 6.5 is most likely to contain soluble salts.

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 34.33%, 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.

Sedimentological Analysis.

The particle size distribution for the raw clay samples (Fig. 2) indicates a clay percentage passing of 45%, a silt range of 12% and a predominantly coarse range. The dorminance of the coarse range could be attributed to a defect in the sample preparation. The high percentage clay passing of 100% of particle size <2μm for the beneficiated clay sample as indicated in the sedigraph (Fig.3) is an indication of the ease with which the silt range can be eliminated for 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.

X-ray Fluorescence 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_2O_3 and SiO_2. They have a combined oxide composition of 78.15%. The loss on ignition of 12.53% is associated with the presence of clay minerals, hydroxides and organic matter. The average values for calcia 0.38%, potash 0.23% and iron 0.68% 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 0.61% must have imparted the medium plasticity property on the clay. The 0.68% Fe_2O_3 content is an indication of an oxidizing environment (Weaver, 1989). This must have resulted in the mild change in the clay color from milk white to light grey upon sintering at 1200℃. The combined value of Al_2O_3 and SiO_2 of about 78.15% coupled with the low alkali content of 0.61% makes the clay suitable for the production of firebricks (Adekanmbi, 2005) and super-heat duty fireclay refractory material (Chesti, 1994).

Mineralogical composition

The X-ray diffractograms for both the beneficiated and unbeneficiated bulk clay samples (Figures 4 & 5) showed two distinct peaks at 2.5^o 2ϴ (d = 7.1Å) and 24.9^o 2ϴ(d = 3.5Å) indicating the dominance of the kaolinite mineral. There were also basal reflections indicating the presence of the halloysite and illite minerals.

CONCLUSIONS

Physico-chemical analyses on Agbaja clay revealed that the clay is in the fireclay class.The low alkali oxide content of 0.61% must have helped impart the intermediate plasticity properties on the clay. The low Atterberg plasticity Index value of 15.45% and the soil activity value of 34.33% are 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 coloration on firing was indicative of the presence of only a small amount ferrogenious mineral. Other minerals present in the clay were halloysite and illite.

Table 1: Physical Characteristics of Agbaja Clay

Plasticity	Unbeneficiated	Beneficiated	Natural Water Content at 115°C (wt%)	Soil Activity (A) (%)	Firing Characteristics	
Liquid Limit	41.90	39.00	7.26	34.33	Temp. °C	Color Change
Plastic Limit	26.00	25.10			115°C	Milk White
Atterberg Plasticity Index	15.90	15.00			1200°C	Light Grey

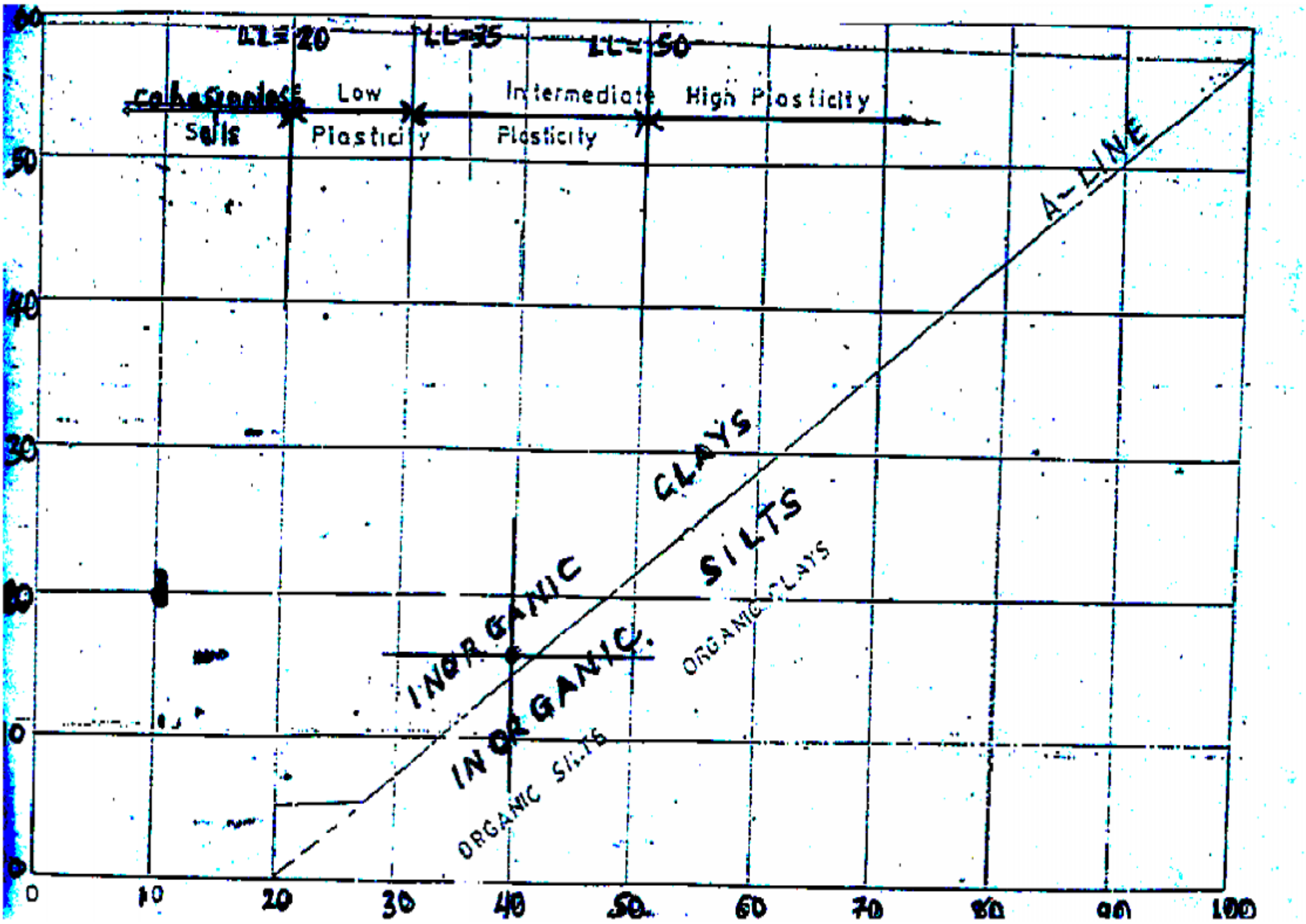
Table 2: Chemical Composition of Agbaja Clay in Comparison with Ranges for Industrial Applications.

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).

Table 3:Minerals Found in Agbaja Clay Sample

Untreated Raw Clay Sample	Treated Clay Sample
Kaolinite	Kaolinite
Halloysite	Halloysite
Illite	Illite



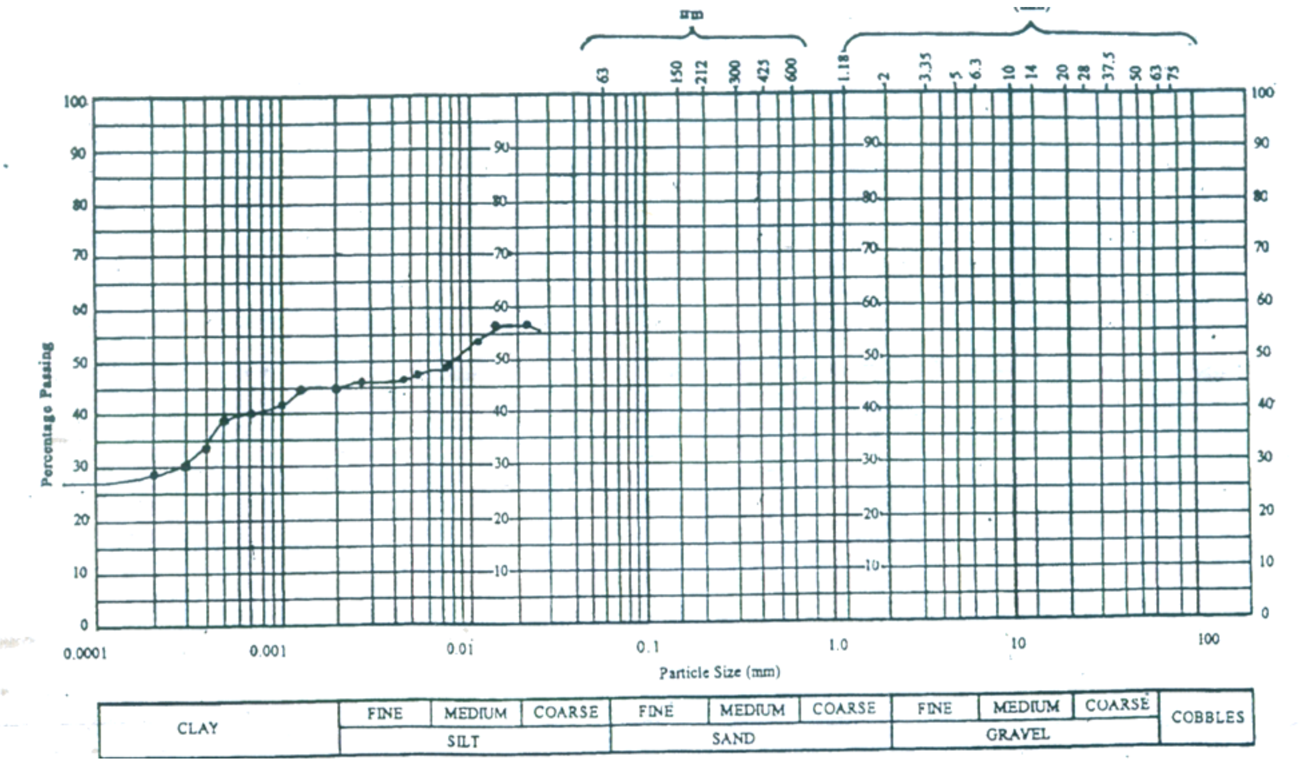


Figure 2. SEDIGRAPH for UnbeneficiatedAgbaja Clay Sample

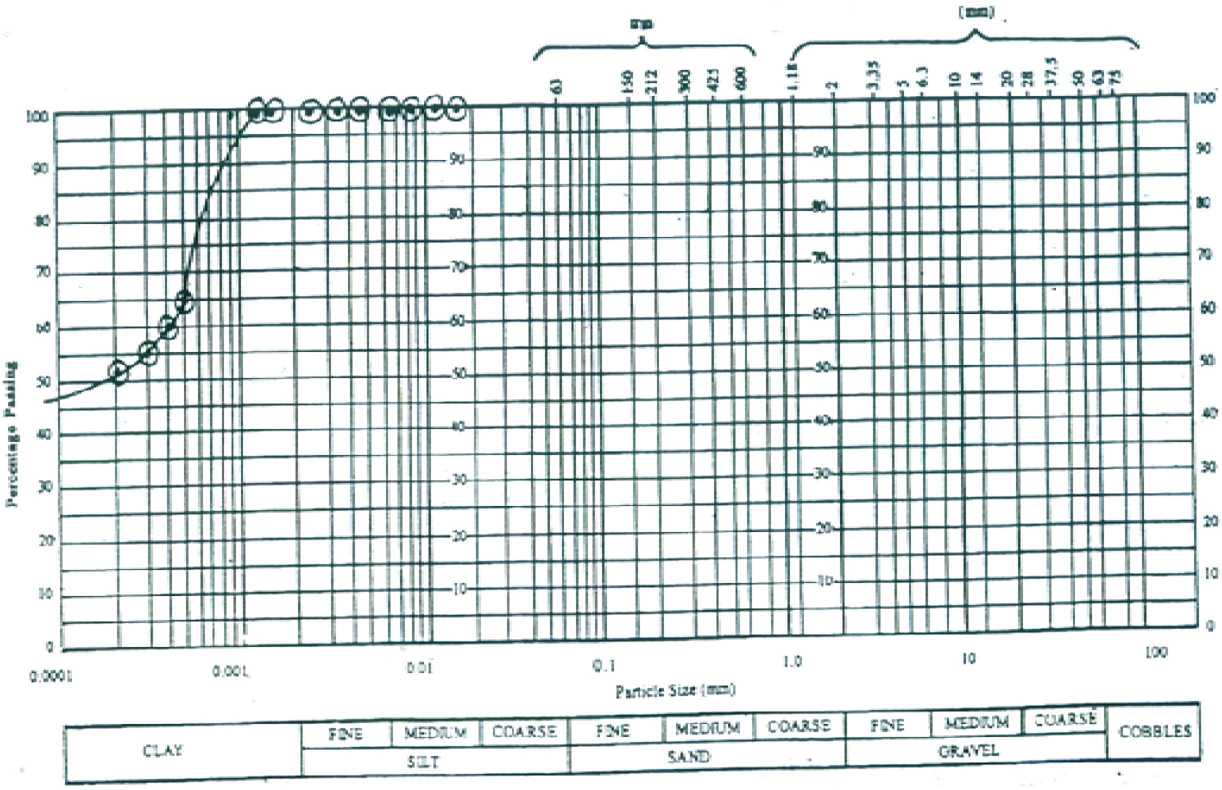


Fig. 3: SEDIGRAPH for Beneficiated Agbaja Clay Sample

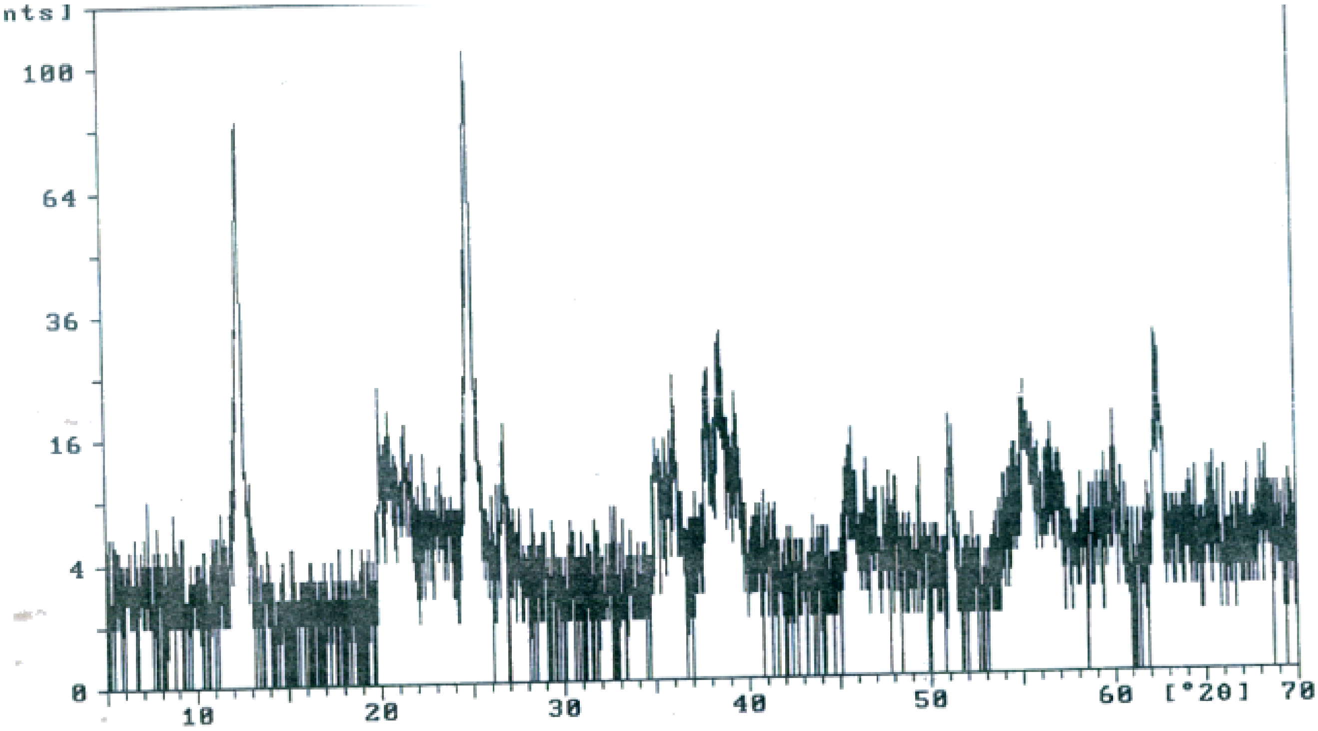


Figure 4. **XRD Diffractogram for Bulk Unbeneficiated Agbaja Clay**

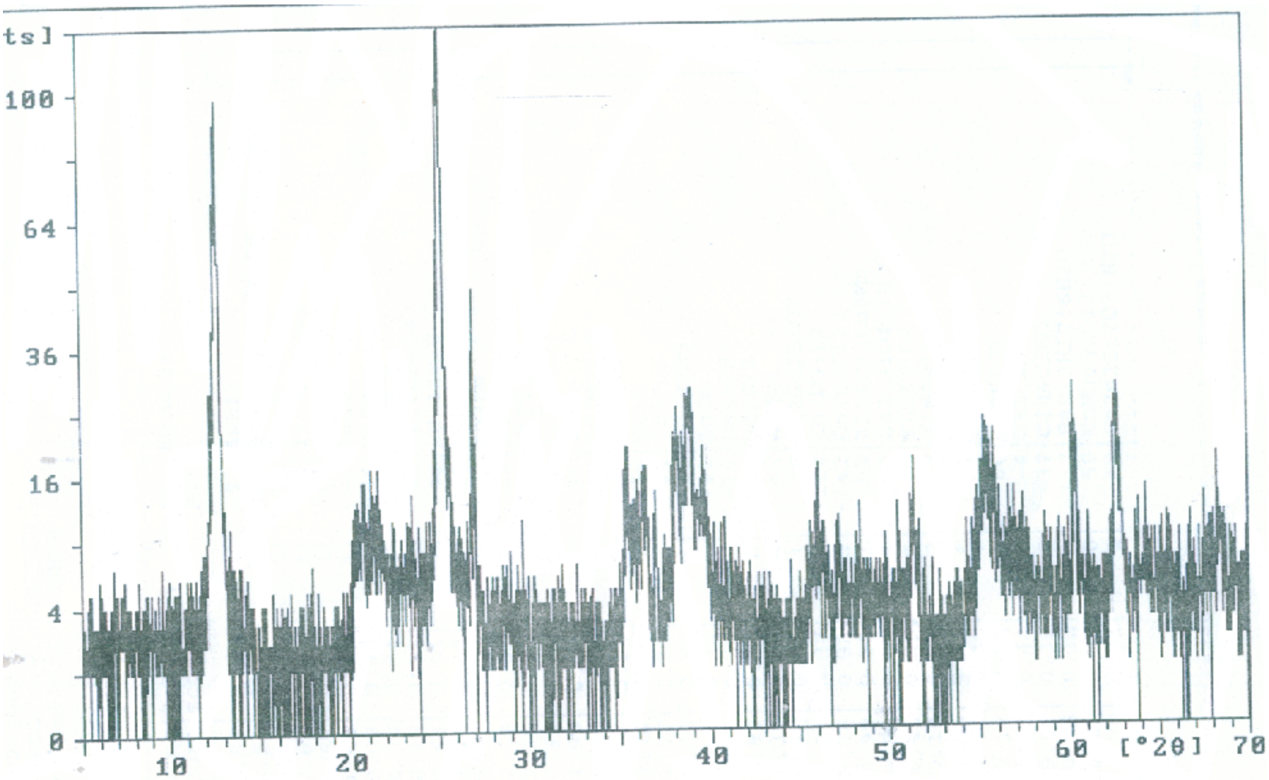


Figure 5. **XRD Diffractogram for Beneficiated Agbaja Clay**

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