

Research Paper

Analysis and Characterization of Kerang Clay Deposit for Industrial Application

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In view of the need to explore the abundant natural resources available for industrial utilization the analysis and characterization of Kerang volcanic clay deposit was carried out with a view to finding its possible industrial application and establishing a bank of its properties. The chemical analysis was carried out using x-ray fluorescence spectrometer while physical properties such as firing shrinkage was determined using sand sedimentation technique, apparent porosity using boiling point technique, cold crushing strength by compressive load technique, bulk density by gravimetric method, thermal shock resistance using single chamber thermal shock equipment and refractoriness by the cone comparison technique. Chemical analysis showed that the clay is composed of Silica (SiO₂) 29.50%, Alumina (Al₂O₃) 15.58%, Potassium oxide (K₂O) 1.28%, Calcium oxide (CaO) 2.43%, Titanium Oxide (TiO₂) 5.49%, Iron oxide (Fe₂O₃) 41.64%

and other oxides in traces. Firing shrinkage was 4.0%, apparent porosity 17.30%, cold crushing strength 236 kg/cm³, bulk density 2.30 g/cm³, thermal shock resistance 2 cycles and refractoriness of <1200°C. The presence of aluminium oxide and iron oxide has a favorable effect on the clay physical properties. The clay is bentonitic due to its aluminium oxide content. It can be used in the metals industry as a binder for moulding sand for casting metals, as drilling mud in drilling for petroleum. It can also be used in engineering works to seal leaks when mixed with water, as well as for potteries and for the moulding of building bricks. Also because of its attractive colour the clay can be used in paint, chalk and paper making industries.

Keywords: Chemical analysis, firing shrinkage, apparent porosity, cold crushing strength, bulk density and refractoriness

INTRODUCTION

Kerang is located in Mangu Local Government Area of Plateau State Nigeria. It is about 80 km from Plateau state capital, Jos. Kerang clay draws its attractiveness from its unique reddish color, and smooth texture. According to Apiam, (1985) clay is a complex mixture whose composition varies widely depending on its geographical location. He further described clay as a natural substance occurring in great abundance being constantly formed on the earth's surface as a result of rock weathering. Thus clay is a material resource of major industrial importance. To indicate the importance of clay in the industrial world, it is only necessary to say that tiles, bricks, pottery, furnace linings to name a few are

almost exclusively formed from the substance. Clay is powdery when dry, plastic when wet and stone – like when baked. Chemically clays are aluminosilicates composed of aluminum (Al₂O₃) and silica (SiO₂) that contain chemically bonded water sometimes with amounts of iron, alkali and alkali earth compounds as well as some organic matter as impurities (Onyeji, 2010). Clays are divided into two categories, residual clay and sedimentary clay. Literature vividly indicates that clay deposits abound in Nigeria, yet the bulk of the clay requirement of Nigeria is imported from United Kingdom, United States of America and Japan (Nnuka and Apeh, 1991). This could be said to be a costly oversight that can

make our nation a perpetual slave to importation of refractories, a material which is quite inadequate and the situation is unacceptable since the development of metals industry and refractories go together. Refractory materials by definition are usually inorganic non-metallic materials supposed to be resistant to heat and can be exposed to varying degrees of mechanical stress and strain, chemical stress, creep formation, thermal shock, corrosion and erosion from fluids, liquid and gases, gas diffusion and mechanical abrasion at various temperature, (Hadyn, 2002). Chemically, they are acidic, basic or neutral. Acidic refractories contain predominantly acid oxides. Basic refractories are made from oxides which are oxygen donors while neutral refractoriness manifests both acidic and basic characteristics (Obikwelu, 1986). Kerang clay has been used as a source of raw material by most local potters and is one of the unidentified clay deposits in Nigeria. Thus if this clay deposit is exploited and properly harnessed, it will no doubt provide internal sourcing of raw materials which will reduce the nations over dependence on importation of materials used in ceramic, chalk and paint industries. This will increase the nation's Gross Domestic Product (GDP). The objective of this work is to characterize Kerang clay so as to determine its suitability for aluminosilicate refractory production and other industrial applications to enable industrialist have access to it as a replacement for imported clays with similar characteristics.

Types of clay

Clay can be classified as either residual (primary) or sedimentary (secondary) clays. Residual clays have remained more or less at the site of the decomposed rocks. They are less plastic than the sedimentary clays and because they have been subjected to fewer erosive forces, their particle sizes are much larger. Sedimentary clays are those that by the action of winds and running water have been transported far from the site of the parent rock. Their particles are very fine and the clay more plastic. According to William and Plummer (1951), clays industrially are classified according to their properties and usage. These classifications include:

Kaolin clay

Kaolinite is a clay mineral part of the group of industrial minerals with chemical composition $\text{Al}_2\text{SiO}_5(\text{OH})_4$. It is a layered silicate mineral with one tetrahedral sheet of silica (SiO_4) linked through oxygen atoms to one octahedral sheet of alumina (AlO_6) (Deer et al., 1992). Rocks that are rich in kaolinite are known as kaolin or China clay. Kaolinite has a low shrink – well capacity and a low carbon – exchange capacity (1 – 15 Meq/100g) (Pohl, 2011). It is soft, earthy usually white mineral

(dioctahedral phyllosilicate clay) produced by the chemical weathering of aluminum silicate minerals like feldspar. In many parts of the world, it is colored pink – orange – red by iron oxide giving it a distinct rust hue. It is generally of low plasticity and high refractoriness (1750-1770°C). The main use of the mineral kaolinite (about 50% of the time) is paper production. Its use ensures the gloss on some grades of coated paper (Murray and Hadyn, 2016). It is also used for fine pottery and porcelain.

Ball clay

Ball clays are sedimentary in origin. Ancient rivers and streams washed kaolinite (formed from decomposed granite) from its parent rock. As the streams flowed from upland areas the mixed with other clay minerals, sands, gravels and vegetation before settling in low-lying basins to form overlaying seams of ball clay. Ball clays usually contain three dominant minerals: from 20-80% kaolinite, 10-25% mica, and 6-65% quartz. In addition, there are other 'accessory' minerals and some carbonaceous material (derived from ancient plants) present. The wide variation both in mineral composition and in the size of the clay particles results in different characteristics for individual clay seams within a deposit. Ball clays are used in many different industries, but in particular form a vital component in ceramic manufacturing. Kaolin ('china clay') produces a very white color when it is fired, but used alone it is brittle and weak and must be mixed with ball clay to produce a workable, malleable raw material. As a result of their sedimentary origin, raw ball clays have a wide range of colors. However, many of them are valued by the ceramics industry for their white-firing properties, which are determined by the levels of iron and other coloring/fluxing oxides within the clay. Ball clays are relatively scarce deposits due to the combination of geological factors needed for their formation and preservation. They are mined in parts of the Eastern United States and from three sites (Selwood et al., 1984) in Devon and Dorset in South West England (David et al., 2006). They are commonly used in the construction of many ceramic articles, where their primary role, apart from their white colour, is to either to impart plasticity or to aid rheological stability during the shaping processes.

Fire clay

Fire clay is a range of refractory clays used in the manufacture of ceramics especially fire bricks. The United states Environmental protection Agency defines fireclay very generally as a mineral aggregate composed of hydrous silicates of aluminium with free silica (U.S Environmental Protection Agency, 1985). It is basically kaolinite with some iron oxides, magnesia and alkaline. It can resist high temperature. It is used for making

refractory products which are used to line surfaces, kilns and crucibles. Fire clays are all clays (excluding bentonite and ball clays) that are used to make items resistant to extreme heat. Nearly all (81%) of fire clay are used to make refractory products (Onyeji, 2010).

Common clay

It is used for bricks, clay pipes, clay floor, wall tiles and other building materials. It contains more impurities than fire clay and does not have a great resistance to heat.

Bentonite

Bentonite is classified as fine grained primary clay. Although chemically like all other clay, it swells excessively turning to a gel. It also has very high shrinkage and stickiness properties. It is clay of high plasticity and is chiefly composed of montmorillonite. The plastic sizes are largely in the colloidal range which undoubtedly contributes to its very high plasticity exceeding that of ball clay. It is possible to get a desired degree of plasticity by mixing bentonite with some ball clay. Bentonite was named after the cretaceous Benton Shale near Rock River, Wyoming, U.S.A (Hosterman and Patterson, 1992). The different types of bentonite are each named after the respective dominate elements such as Potassium (K), Sodium (Na), Calcium (Ca) and Aluminium (Al).

Bentonite usually forms from weathering of volcanic ash, most often in the presence of water. For industrial purposes two main classes of bentonite exist. Sodium and calcium bentonite. Large deposits of bentonite clays have been identified in various parts of Nigeria. However, the occurrence of pure bentonite (Wyoming bentonite) has not been confirmed, but there are reports of highly montmorillonite clays in Borno, Yobe, Adamawa, Abia, Anambra, Edo, Imo, Ebonyi, Akwaibom and Cross – River States of Nigeria (Ihom et al., 2006). In 2011 the United States of America was the top producer of bentonite with almost one – third world share followed by China and Greece (Brown et al., 2013). Bentonite's ceramic significance is in increasing plasticity, and its high iron oxide content which limits its usage in the ceramic industry (Brown et al., 2013). It finds its application in the metals industry as molds for casting metals and as drilling mud in drilling for petroleum. Bentonite that expands when mixed with water is used in engineering work to seal leaks.

Fullers earth

This is composed of montmorillonate and is high in magnesia. In other words, Fullers earth is any clay that has the capability to decolorize oils or other liquids

without chemical treatment (Hosterman and Patterson, 1992). Modern uses of Fullers earth include absorbents for oils, grease, pet litter or animal waste management, pesticides and other products.

MATERIALS AND METHOD

The clay sample for this work was obtained from Kerang volcanic clay deposits in Mangu L.G.A. of Plateau State. All the analysis and characterization were conducted at the National Metallurgical Development Centre (NMDC); Jos. Equipment used for the tests among others included a standard sand sample rammer, sand mixer, universal sand strength testing machine, baking oven and a carbolite furnace. The sample was weighed, crushed, ground, milled sieved and measured out into proportions for the various experiments to be performed.

Determination of chemical composition

The chemical composition of the clay was determined using x-ray fluorescence spectrometer (XFS). This is a non-destructive analytical technique used to identify and determine the concentration of elements present in solid, powdered and liquid samples. ED - XFS is capable of measuring all elements from beryllium (Be) to uranium (U).

Sample preparation

The sample was ground and sieved to 75 μ m particle size. 4g of the sieved clay particles were intimately mixed with 1g of lithium tetraborate binder ($\text{Li}_2\text{B}_4\text{O}_7$) and pressed to a mould under pressure of 10-15 tons per metre square into pellets. The pressed pellets were dried at 110°C for 30 min. in an oven to get rid of absorbed moisture and were finally stored in desiccators for analysis.

Analysis

The spectrometer was switched on and allowed to warm up and also to stabilize the optics and the X-ray tube. It was then calibrated to determine the expected elements present in the sample. The sample was run using the prepared program calibration and the concentrations of the elements present in the sample were automatically calculated and displayed by the spectrometer.

Determination of firing shrinkage

Firing shrinkage was determined using sand sedimentation test method. The clay sample was

moistened with water to the point of wedging which implies that the moistened clay materials remained packed into a ball until intentional vibration caused the mixture to flow. The wedge sample was cast into brass molds. The clay bar was prepared and the original (initial) length was marked on the sample. The final length after the clay had been fired was recorded. The firing shrinkage was then calculated from the expression:

$$\text{Firing shrinkage: } F_s = (A - B) \times \frac{100}{A} \quad (1)$$

Where A = Initial length

B = Final length

Determination of cold crushing strength of the clay

The cold crushing strength was determined using the compressive load technique according to BS EN ISO 895: 2006 test method. A cube was made from the clay. The length and breadth of the sample were measured. A cardboard sheet not exceeding 0.63 cm in thickness was placed between the platens of a hydraulic press and the bearing. The faces of the test piece were placed centrally on the platen. The load was applied until the test piece failed to support the load. The maximum recorded load was taken as the crushing load. The cold crushing strength (CCS) was calculated using the formula:

$$\text{CCS} = \frac{M}{A} \quad (2)$$

Where

CCS = Cold crushing strength

M=Mass of the sample

A=Surface area

Determination of bulk density of the clay

Bulk density was determined using gravimetric method. The sample was formed into a cylindrical rod of 2.5 cm diameter and 1.5 cm height. The weight (W_1) was measured. 100 g of clean mercury was poured into 100ml beaker and placed on the balance. The balance was adjusted until the gram scale read zero. The saddle was lowered into the mercury by means of the hand wheel and locked with the bridge locking screw. The micrometer was adjusted until the pointer touched the surface of the mercury. The weight W_2 was taken from the balance reading. The saddle was raised and the specimen removed. The volume of the sample was given as:

$$\text{Volume} = \frac{W_2}{d} \quad (3)$$

Where d=density of mercury

The temperature of mercury used in the experiment was 23°C and the corresponding value of density of mercury used for the calculation was 13.5386g/cm³. The bulk density was calculated from the expression.

$$\text{Bulk Density} = \frac{W_1 + d}{W_2} \quad (4)$$

Determination of thermal shock resistance of the clay

Thermal shock resistance was determined using a single chamber furnace. Test pieces of the clay bricks were thoroughly dried and placed in the furnace (at room temperature) and heated at a rate of 5°C/min up to 1200°C. The specimens were kept at the testing temperature for 30 min with a pair of tongs previously warmed in the furnace for a short time. The test pieces were then placed on a cold fired brick in a position free from draught. After the test pieces had been cooled in this way for 10 min, they were returned into the furnace for a further 10 min and the cycle was repeated until failure occurred.

Determination of the refractoriness of the clay

The clay sample was formed into simple cones of 1.27cm base diameter and height 3.81cm. The cones were mounted on refractory base along with several other standard cones of the same dimension and standard compositions. The cones were heated at a rate of 5°C/minute in an oxidizing atmosphere in the furnace until the test cone squatted (bent) over its own weight. After cooling, the test cone was compared with the standard cone. The test material was taken to have pyrometric cone equivalent of the standard cone whose behavior most resembled that of the test cone.

Determination of apparent porosity

Apparent porosity test was carried out using the boiling point method. From a conveniently made clay brick, a cube of 2.5 x 2.5 cm was cut and dried in an oven at 110°C to a constant weight (D). The dried sample was suspended in distilled water such that the sample did not touch the bottom or sides of the container (300 ml beaker). The water was boiled for two hours while the sample was still suspended in it. The sample was then cooled to room temperature and its soaked weight (s) was noted. It was then removed from the water and the water wiped off its surface by lightly blotting with a wet towel and its suspended weight (W) in air was determined. The apparent porosity (P) was then calculated by the formula:

$$\text{Apparent porosity, } P(\%) = \left(\frac{\text{Soaked Weight}(W) - \text{Dry Weight}(D)}{\text{Soaked Weight}(W) - \text{Suspended Weight}(S)} \right)$$

$$\text{Thus, } P = \frac{(W-D)}{(W-S)} \times 100\% \quad (5)$$

RESULTS AND DISCUSSION

The results from the chemical analysis are given (Tables 1 and 2). Results of chemical composition of the clay are as shown in (Table 1).

Table 1. Results of chemical analysis.

Compound	Percentage (%)	Composition
Al ₂ O ₃	15.58	
SiO ₂	29.50	
K ₂ O	1.28	
CaO	2.43	
TiO ₂	5.49	
Fe ₂ O ₃	41.64	
V ₂ O ₅	0.20	
Cr ₂ O ₃	0.19	
MnO	0.47	
TNiO	0.19	
aCuO	0.13	
bZnO	0.04	
lEu ₂ O ₃	0.25	

Table 2. Results of physical properties test conducted on sample.

Properties	Values
Cold crushing strength (CCS)	23 kg/cm ²
Bulk density (g/cm ³)	2.30 g/cm ³
Apparent porosity (%)	17.30%
Firing shrinkage (%)	4.0%
Thermal shock resistance	2 cycles
Refractoriness	<1200°C
Colour	Moderate brown

The result show a Silica (SiO₂) content of 29.50%, Aluminium Oxide (Al₂O₃) of 15.58%, and Iron Oxide (Fe₂O₃) content of 41.64%. The presence of aluminium oxide and iron oxide in the soil has a favorable effect on the soil physical properties by increasing aggregate stability, permeability, friability, porosity and hydraulic conductivity and reducing swelling, clay dispersion, bulk density and modulus of rupture (Robert, 2008). This also shows that the clay can be used as a source of iron considering the high content of iron oxide. Other oxides are in minor quantities. The result shows that the percentage of the oxides present is 97.39% which does not sum up to 100%. The difference may be due to traces of other oxides too infinitesimal for detection which may have been removed during pretreatment. The colour of the clay sample is moderate brown as shown in (Table 2). This could be attributed to the high iron oxide content. The ferrous oxide impacted brown colour to the samples

on firing due to conversion from ferrous to ferritic compound. The colour is considered useful for the manufacture of flower pots and earthen wares. The clay may also be used in paint, chalk and ceramics processing industries. The refractoriness was estimated to be <1200°. Thus the clay may be used in processing refractory bricks needed for lining of the walls of furnaces for smelting certain non-ferrous metals like copper, Zinc aluminum etc. It can also be used for soaking pits, kilns, ladles, ovens and heat treatment furnaces. The porosity of the clay was estimated to be 17.30% and bulk density 2.30 g/cm³. Shrinkage, porosity and bulk density are interrelated quantities. The more the material shrinks, the less porous it is and hence the denser. The results shows that the thermal shock resistance of the clay is 2 cycles, meaning it can only withstand two thermal cycles before it cracks.

Conclusion

The chemical analysis result shows that Kerang clay has a high content of iron oxide and aluminium oxide which suggest it to be bentonite with free quartz present and thus has usefulness in production of material such as ceramics, furnace linings, potteries, building bricks, electrical insulators, paint, foundry mould making as well as abrasives wares. There is thus the need for a geological survey to determine the extent of the clay deposit.

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