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Research Article

DETERMINATION OF THE CHEMICAL COMPOSITIONS OF CLAY DEPOSITS FROM SOME PART OF SOUTH WEST NIGERIA FOR INDUSTRIAL APPLICATIONS

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Abstract

Clay is one of the major raw materials in ceramics, paint and paper industries. In this paper, a report is given on the chemical composition of clay deposits in Ilaro and Ikorodu, South West Nigeria and their suitability as raw materials in the above mentioned industries is suggested by comparison of their composition with industry standards. The clay samples were activated with H₂SO₄ and their moisture content was determined. The mineral content of the clays was determined using atomic absorption spectroscopy, which showed significant presence of Si, Al, Fe, and Ti. The morphology of the clays was studied using scanning electron microscope (SEM/EDX) in combination with X-ray analysis. The investigation revealed the agglomeration of the particles of quartz and rutile on the surface structure of the activated clays. The results obtained from their observed properties and chemical compositions indicate that these clays are suitable for use in the ceramics, paint and paper industries. This proposition is supported by reduction in moisture contents of the activated clay samples from both Ilaro and Ikorodu.

Keywords: Clays; Morphology; Ceramics; Refractory materials; Chemical composition

Introduction

Clay minerals from different regions have different chemical compositions and physical properties and so the industrial application of a clay mineral is dependent on its intrinsic chemical and physical properties. As raw materials in ceramics, paint, paper and refractory industries, clays need to be worked upon to satisfy the conditions to be met in these industries. A clay material is considered suitable for use, if it has high resistance to wear, high strength at high temperature, good chemical stability and good electrical insulation properties (Guggenheim and Martin, 1995). For example, a clay mineral can be used to make a refractory material. A refractory is a material that will withstand high temperatures sufficient to permit its use in a furnace lining or other location where it will be exposed to severe heating. Clay minerals are used as coating on paper to produce whiteness and to allow the proper absorption of ink.

Clay plays important roles in the production of ceramic articles and its products. A ceramic is an inorganic non-metallic solid made up of either metal or non-metal compounds that have been shaped and then hardened by heating to high temperatures. Ceramic can be heat-resistant,

non-metallic, inorganic solids that are made up of compounds obtained from non-metallic and metallic elements (Inegbenebor et al., 2003; Cultrone et al., 2004; Gonzalez-Garcia et al., 2010; Liu, 2007; Njoya et al., 2006; Velde, 1992). Although different types of ceramic can have very different properties, commonly used ceramics are brittle, corrosion-resistant and hard. These features have led to the use of ceramics in almost every aspect of modern day activities (Njoya et al., 2006; Velde, 1992; Brown, 1955).

Commercially, the most important clays are kaolinite, Al₂Si₂O₅(OH)₄ and bentonite, a rock consisting mainly montrimorillite of smectite group, monoclinic silicate of general formula X_{0.3}Y_{2.3}Z₄O₁₀.nH₂O; X is exchangeable ion, like Ca²⁺, Li, Na; Y =Al, Cr⁺³, Fe⁺², Fe⁺³, Li, Mg, Ni, Zn, and Z =Al, Si. There are over thirty types of clay but in pottery these types are divided into the three main classes of earthenware (Brown, 1955; Meseguer et al., 2009; Zimmerman and Weindorf, 2013). The categories of clay are based on how long and at what temperature the clay is fired in order to reach maturation, or its optimal hardness. Each category includes clays with different colors and ratio of work rate. Differences in colour of clays are caused by

gauge element/minerals. For instance, high levels of iron in clays impart negatively on the plasticity and porosity of the clay. Also the clay could be hard, corrosion-resistant and brittle. The aim of this paper is to look at the suitability of the clay in these areas in term of their morphology, properties such as moisture content for the materials in ceramic, paper and paint industries.

Methodology

Collection and Preparation of Clay Samples

Bulk clays were collected from two different zones in South-Western States of Nigeria, Ilaro in Ogun State and Ibeshi/Ikorodu, Lagos State. The sites were dug to a depth of 1.5 m in order to get homogeneous samples. The samples were air-dried, sieved to size less than 149 μm . For easy identification these samples have been designated, CIL for clay collected at Ilaro, and CIK, for clay collected at Ikorodu.

Activation Method for Morphology Studies of Clay Samples

The clay samples obtained from CIL and CIK were powdered and sieved to particle size of 250 μm and later calcined between 550 – 600°C. The samples were acidified using (0.1% w/v) dilute sulfuric acid. Each of the clay sample (150 g) was placed in different beakers and distilled water (50 mL) was added to make paste slurry. Dilute acid (150 mL) was added to soak the paste for 1 h at a controlled temperature range of 80 – 100°C. This was later dried at 120°C for 12 h.

Quantitative Chemical Analysis

Quantitative determination of the mineral constituents such as, SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , TiO_2 , and Na_2O of the clay samples was undertaken using Atomic Absorption Spectrophotometer (S4AASystem GE712118). The physical characteristics of importance such as moisture density were also determined. Both the activated and raw clay samples (200 g) were each mixed with distilled water (120 mL) for 24 h before making into molds using cubic-shaped metallic mold.

Moisture Content Determination

After the mold-process, the moisture content was determined using an electrical-balance at 105°C until constant mass was attained, this was about 2 h. The relative plasticity was determined with the cylindrical test pieces. The original height, H_o of the test pieces was obtained by the use of the vernier caliper (taking an average of three readings each). Afterwards, a manual plastometer machine was used to deform the test pieces. Average of three side-deformation heights, H_i and the relative plasticity was then calculated using the relationship: Relative Plasticity = H_o/H_i .

Chemical Composition

The decrease in mass during firings was the 'Loss on ignition' (LOI), which was determined by placing the finely

powdered clay in a muffle furnace at 1000°C for 1.5 h. The LOI was calculated using the equation: $LOI(\%) = \frac{w_f - w_i}{w_i}$; where w_f and w_i are the final and initial mass respectively of the clay sample.

Chemical compositions of both the raw and activated clays were determined by X-ray fluorescence (XRF), using a Philips PW2400 XRF spectrometer. The X-ray diffractometer (XRD) was carried out with Philips PW 3710 powder diffractometer $\text{Cu-K}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation and a Ni filter, with a vertical goniometry at room temperature. The raw and activated clays were held with sample holder and ground before being mounted on glass disc for Scanning Electron Micrograph (SEM). This was carried out using an XL30 S-FEG SEM unit with a 10 kV accelerating voltage (Buhrke et al., 1998; Odo et al., 2009; Komadel et al., 1990; Markozic and Van Grieken, 1993). The samples were 'gold-coated' at 1 kV and 14 mA for 5 minutes followed by sample analyses at 20 kV.

Results and Discussion

The percentage composition of minerals in CIL and CIK are summarized in Table 1, which shows that CIL and CIK contain a lot more minerals required in standards for ceramics, refractory, glass, paper paint and Tiles (Odo et al., 2009).

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in CIL and CIK is 1.3 and 2.3 respectively. From the table, it can be seen that CIL and CIK contain about equal amounts, within experimental error, of SiO_2 and Al_2O_3 as recommended for ceramic, paper and paint and within the range for refractory. These ratios are also within the range recommended for clays that are suitable for use in zeolite synthesis (Breck 1974). Both CIL and CIK contain 0.5 and 0.6 the amount of SiO_2 respectively and 0.4 and 0.3 the amount of Al_2O_3 respectively of the standard composition found in glass. Based on these values for SiO_2 and Al_2O_3 , these clays would not be suitable for use in the glass industry. The Fe_2O_3 content is very much higher than the content recommended for ceramic, refractory, glass, paper and tile, but only slightly higher than that required for paint. With this observation in the Fe_2O_3 content, it could be suggested that both CIL and CIK would be suitable for use in paints. Both our clays, CIL and CIK contain TiO_2 with values of 2.6 and 1.3 respectively compared with 1.6 required in tile materials.

The physical characteristics of importance, such as moisture density were also determined as shown in Table 2. It can be seen that there was a decrease in the moisture content after activation.

Fig. 1 and Fig. 2 show comparative analyses of X-ray diffraction spectra for CIL and CIK, which reveal that CIL is composed of kaolinite and quartz as compared to quartz and rutile for CIK.

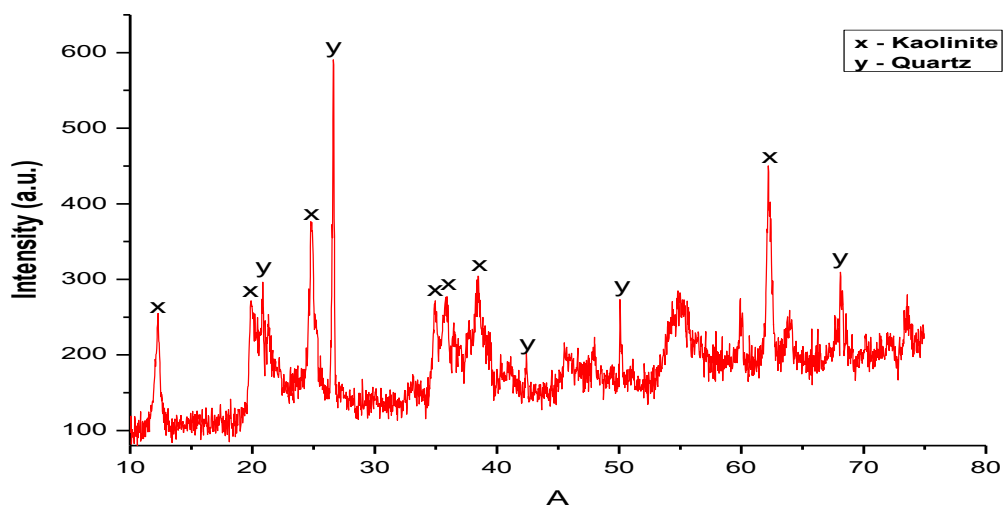
Table 1: Chemical Composition of Clay Samples (CIL and CIK) from South West Nigeria Clay Deposits and the Standard Requirements for industrial application of Clay

	CIL	CIK	Ceramic ^a	Refractory ^a	Glass ^a	Paper ^a	Paint ^a	Tile ^a
	(mg/g)							
SiO ₂	43.5	54.5	60.5	51 - 70	80 - 95	45 - 48	45 - 48	70.0
Al ₂ O ₃	34.2	24.6	26.5	25 - 44	80 - 95	34 - 38	37 - 39	19.0
Fe ₂ O ₃	16.6	15.4	0.5 - 1.2	0.5 - 2.4	2 - 3.0	0.3 - 0.6	13.4 - 13.7	1.6
CaO	0.2	0.2	0.2 - 3.0	0.2 - 2.0	4 - 5	0.03 - 0.6	0.03 - 0.6	0.2
K ₂ O	0.1	0.2	-	-	-	-	-	2.0
TiO ₂	2.6	1.3	-	-	-	-	-	1.6
CuO	0.2	2.2	-	-	-	-	-	-
V ₂ O ₅	0.1	0.2	-	-	-	-	-	-
Cr ₂ O ₃	0.1	0.1	-	-	-	-	-	-
Ag ₂ O	1.5	1.6	-	-	-	-	-	-
LOI	6.3	4.6	7.8	1.5	-	-	-	5.4

a = Standard (Odo et al., 2009)

Table 2: The Moisture Content of both Activated and Raw Samples from South West Nigeria clay Deposits.

Sample	Raw Moisture %	Activated Moisture %
CIL	32.56	22.84
CIK	38.64	21.34

**Fig.1:** X-ray diffraction spectrum (XRD) for CIL.

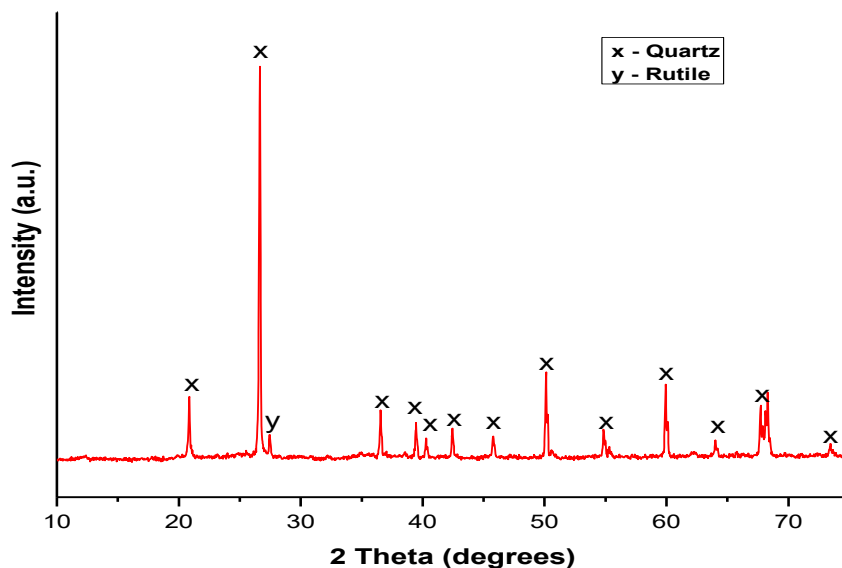


Fig.2: X-ray diffraction spectrum (XRD) for CIK

The microstructure was studied by SEM (1000x, 15kV, 268 μm) for raw and activated clay samples of CIL and CIK. The images were obtained at different magnifications as shown in Fig. 3 – 8. The micrographs are as shown in Fig. 3 – 6. It can be seen that there are differences in the pore sizes (compare SEM images for CIL, Fig. 5 and 6), which could be the result of leaching out of impurities and trace metal oxides from between the tetrahedral silicate planes

and the octahedral alumina planes. The suggested change in the structure due to activation might lead to closer packing of the planes thereby creating a morphology indicated by coarser and heterogeneous patches, Fig. 3 (CIK) and Fig. 5 (CIL). The activated sample figure 4 (CIK) showed more agglomeration than Fig. 6 (CIL). In Fig. 7 and 8, the effects show more harness and homogenization at above 3000x and 70 – 90 μm for the activated samples CIL and CIK.

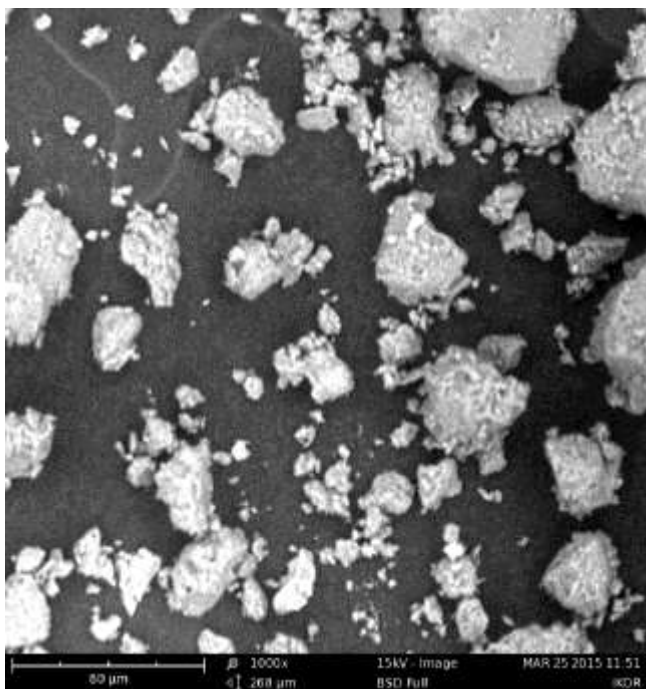


Fig 3: SEM Image of CIK (1000x, 15KV, 268 μm) (Raw)

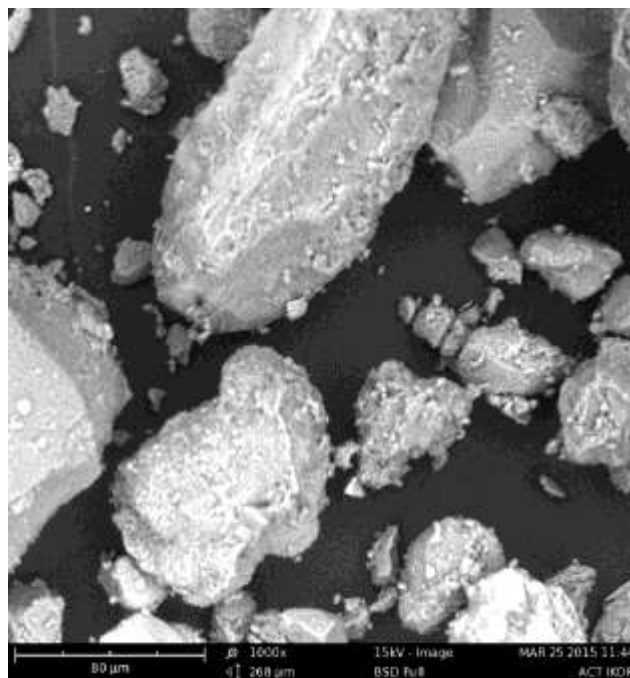


Fig 4: SEM Image of CIK (1000x, 15KV, 268 μm) (Activated)

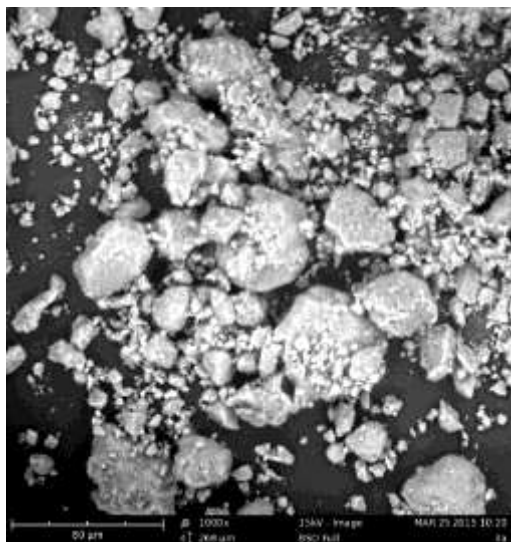


Fig 5: SEM Image of CIL (1000x, 15KV, 268 μm (Raw))

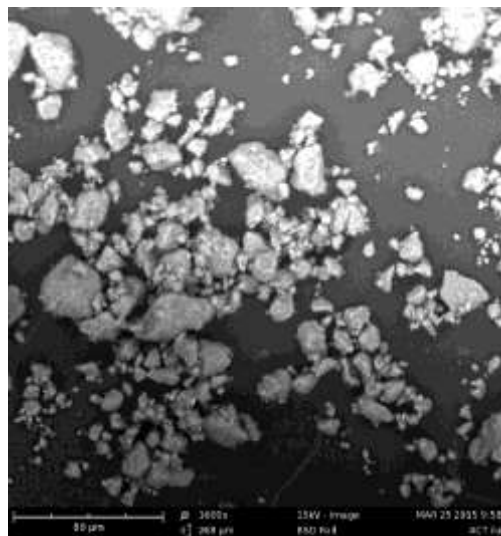


Fig 6: SEM Image of CIL (1000x, 15KV, 268 μm (Activated))

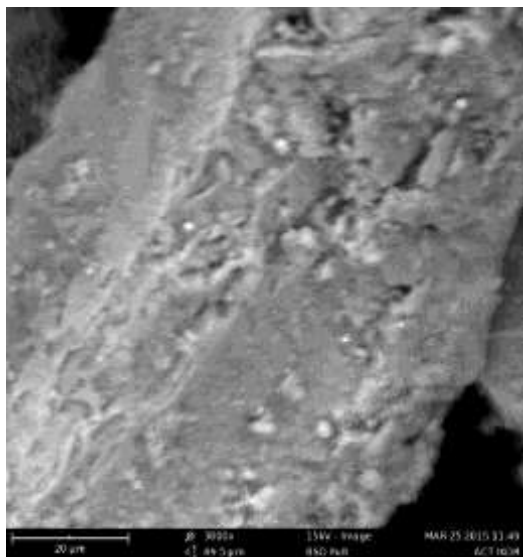


Fig 7: SEM Image of CIK (3000x, 15KV, 89.5 μm, (Activated))

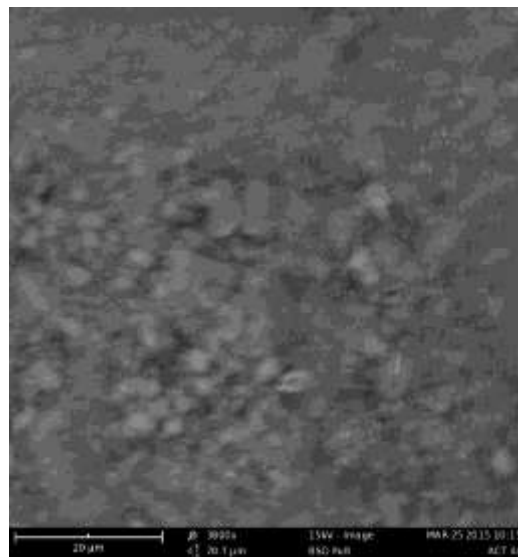


Fig 8: SEM Image of (3800x, 15KV, 70.7 μm (Activated))

The raw sample has a smaller size of particles. The activated clay cluster together which reduces the pore space thereby the porosity will be reduced. This will promote the sample of the clay to be stronger in application.

Conclusion

The clays CIL and CIK have shown promise as raw material candidates for industrial application according to the chemical composition result obtained. The activation of the clay samples caused the agglomeration of the particles, which may invariably reduce the porosity and increase thermal stability. The implication of such, promotes the clay to be stronger in which application it finds itself in the industries. This will help the clay to withstand mechanical applications during their usage in the industry due to coherency of the grains.

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