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Characterization and Value Enhancementof Some Nigerian Refractory Materialsfor Thermal Insulation

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Abstract:*The characterization and value addition to some Nigerian clay deposits; Ijapo Estate, Akure in Ondo State, Ire Ekiti in Ekiti State and Ilesha in Osun State have been carried out. The characterization was done by employing four different techniques on the clays in the as-mined states. The relative proportions of the constituent elements, the morphology and the phase identification of the clays were determined by using X-Ray Fluorescence (XRF), Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS), X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) analyses. The clays were prepared for the analyses by using the standard procedures and the results obtained were compared to confirm the consistency and reliability of the different methods employed. The results obtained revealed the various desirable (CaO, S_iO_2 and Al_2O_3) and deleterious (Fe_2O_3, K_2O and MgO) compounds contained in the clays, in the various proportions. The clays were then purified hydrometallurgically at a predetermined condition; 1.2 mol/dm^3 at 30 °C for 30 min and 200 rev/min in order to remove the iron content which had been identified for being responsible for lowering the melting temperatures of the clays. The purified clays were again characterized using the TEM and XRF analyses to confirm the extent of iron removal. Purified Ire Ekiti clay which responded best to purification was formed into samples containing 5 – 40 % alumina cement, 1-5 % woodflour, fired at varying temperatures of 900 °C, 1100 °C, 1300 °C and 1500 °C and tested for some important insulating properties such as permanent linear change, modulus of rupture and permeability. Purified Ire Ekiti clay containing 10 % alumina cement and 3% woodflour exhibited a good combination of the required properties of a good thermal insulating material.*

Keywords: *characterization, clay, constituent elements, hydrometallurgy and insulation.*

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I. Introduction

Clays are hydrous alumino-silicate ($Al_2O_3 \cdot 2\text{-}SiO_2 \cdot 2H_2O$) and are abundant fine earthly powders produced by the weathering and disintegration of granite and feldspathic rocks [1,2] Depending on the atmospheric and geological condition of deposition, as well as the degree of alteration of the clay, iron (hydr) oxides (usually Fe^{3+} forms) are commonly precipitated or adsorbed to the clay surfaces or admixed as a separate phase [3,4,5]. These iron (hydr) oxides make much of the clays unusable for high temperature engineering applications due to insufficient whiteness [6], reduction of thermal stability and reduction of refractoriness of products [7,8].

As a result of the detrimental role of iron oxide in clays, the quality of clay can be said to be measured in terms of iron content [5,7,8,9]. Some researchers have developed different physical and chemical techniques and recently, microbiological, with the purpose of removing the ferric iron present as oxide or hydrated oxide in the clays. These techniques generally include magnetic separation, froth flotation, selective flocculation, size separation by hydrocyclones and leaching with inorganic acids [6].

More so, earlier works on various Nigerian clay deposits have shown many of them to be unsuitable for refractory applications in the as-mined states. They are either high or low in one or more of the important refractory properties desired for good refractory works, or they are completely lacking in them [8,10,11]. The unsuitability of the local clay deposits for refractory works in the as-mined states and the desire to develop and apply them for high quality engineering works has therefore prompted the need for this work. However, in order to preserve the crystal structure of the clay, hydrometallurgical purification, using an organic acid (oxalic acid) was employed following comprehensive characterization techniques that adequately revealed the amount of iron oxide present in the clays.

II. Materials And Method

The materials and equipment used were raw clays from Ijapo, Akure in Ondo State, Ilesha in Osun State and Ire Ekiti in Ekiti State, oxalic acid (99.8% purity), alumina cement (Secar 71), atomic absorption spectrometer (AAS) machine (model Spectre AA 220 FS), X-ray fluorescence (XRF) machine (model ARL 8410), scanning electron microscope (SEM) model JEOL 840 and coupled with an EDS analyzer, X-ray diffraction (XRD) machine (model Philips PW 3710 with PW 1752 graphite monocromator), sieve size analyser (Microtrac FLEX 10.5.4), Labcon shaking incubator (models 3081U and 5082U), Carbolite furnace, Rawwley Sussex jaw crusher and grinder.

2.1 Preparations of Samples for Analysis

Large quantities of clays as mined from the sites were washed in water in order to remove the deleterious particles by decantation. Water was then drained from the clay slurry using a plaster of Paris (P.O.P.) mould. The recovered clays were then dried in the sun for three days and again in the Carbolite furnace at 90 °C for 8 hours. The dried clays were finally jaw crushed, ground in a Rawwley Sussex grinder and sieved to 100 µm [12]

2.2 Characterization of Clay Samples

Analyses of the clays were carried out using XRD, SEM/EDS, TEM and XRF according to the standard procedures [5]. The results are presented in Figures 1 – 9 and Tables 1 and 2.

2.3 Purifications of Clay Samples

The clays were treated hydrometallurgically in accordance to[8,13,14]. The clay residues were then dried in the Carbolite furnace at 90 °C, crushed, ground and sieved to 100µm [12,13,14] for subsequent tests.

2.4 Preparation of Samples for Performance assessment

Samples with total mass of 150 g each, containing purified clay, varying quantities (5, 10, 15, 20, 25, 30, 35 and 40 %) of high alumina cement (Secar 71), 1 – 5 % of wood flour and 10-15 % of deionized water were formed into cylindrical (50mm diameter x 50 mm high) shape. The samples were dried in air for 24 hrs and later in the oven at 110 ºC for 48 hrs. Some selected samples, after drying at 110 ºC were again taken for firing in the furnace at 900 ºC, 1100 ºC, 1300 ºC and 1500 ºC. The fired samples were subsequently tested in accordance with the American Standard for Testing and Materials (ASTM) for the following properties; permanent linear change, modulus of rupture and permeability. The results are as presented in Figures 10 - 12 respectively.

III. Results And Discussion

The results of the various characterization techniques and the performance evaluation of the prepared firebricks are as presented in Figures 1 to 12 and Tables 1 and 2.

3.1 X-Ray Diffraction (XRD) Analysis

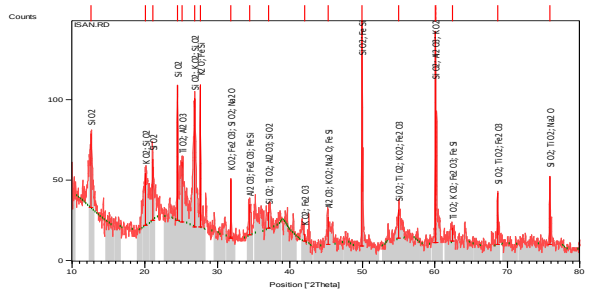


Figure 1: X-ray diffraction pattern of Ijapo clay

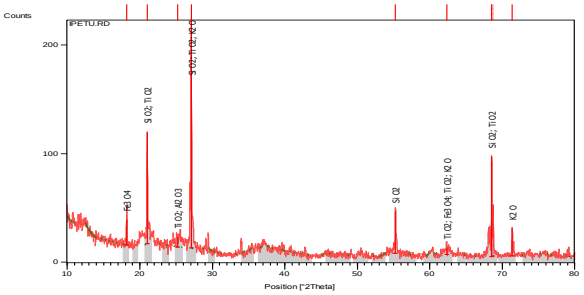


Figure 2: X-ray diffraction pattern of Ire Ekiti clay

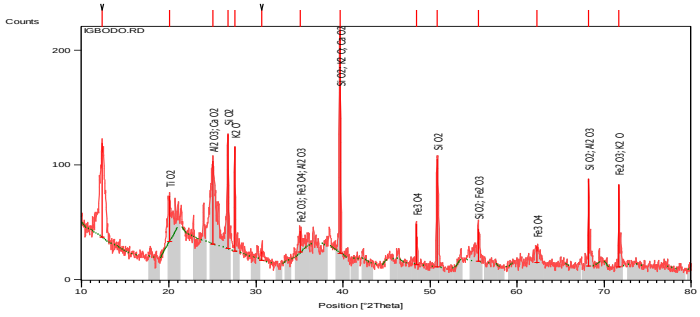


Figure 3: X-ray diffraction pattern of Ilesha clay

The various X-ray diffraction patterns obtained for XRD analysis of the clay samples are as presented in Figures 1–3. These were done for qualitative analysis of the clays. The patterns show sharp high peaks for SiO_2, Al_2O_3, Fe_3O_4 and sharp but shorter peaks for K_2O, MgO, MnO, Na_2O and CaO. Some other oxides were also present but in very negligible proportions.

3.2 Scanning Electron Microscopy (SEM)

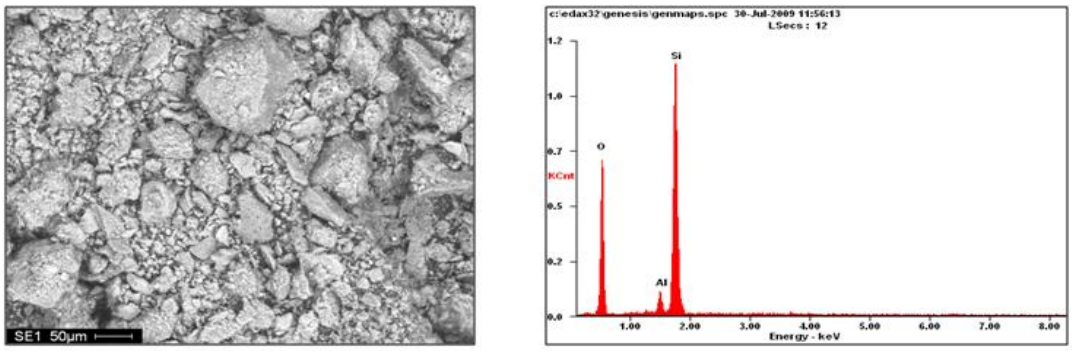


Figure 4: SEM Micrograph and the spectral of Ijapo Clay Showing the Morphology and relative abundance of the constituent elements in the Clay.

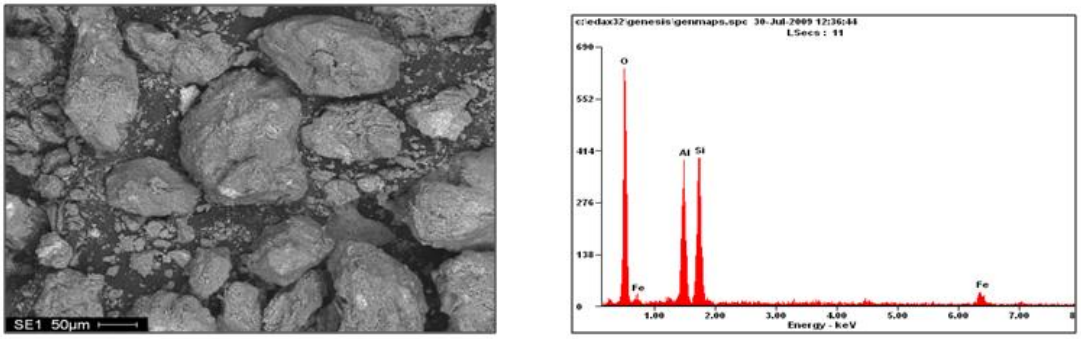


Figure 5: SEM Micrograph and the spectral of Ire Ekiti Clay Showing the Morphology and relative abundance of the constituent elements in the Clay.

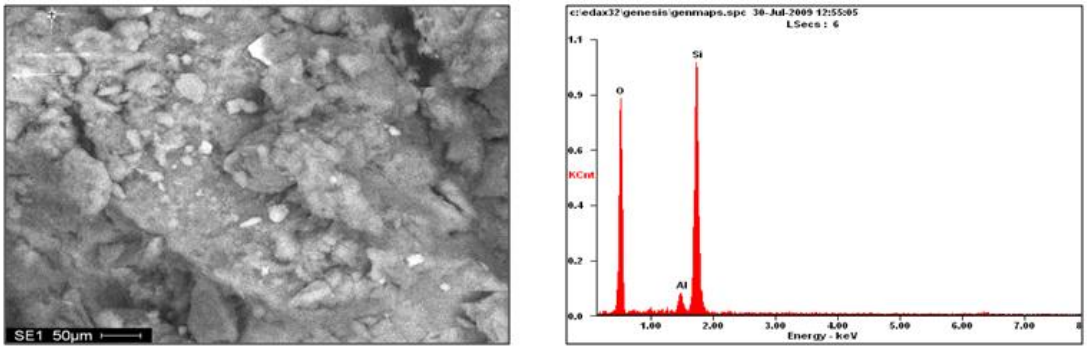
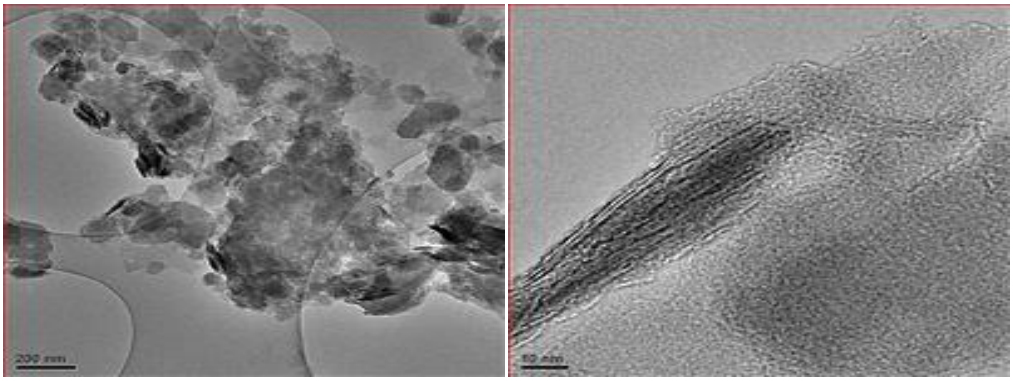


Figure 6: SEM Micrograph and the spectral of Ilesha Clay Showing the Morphology and relative abundance of the constituent elements in the Clay.

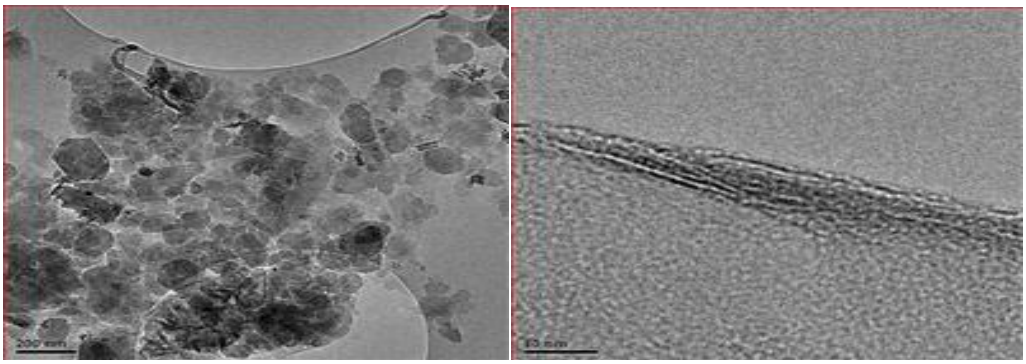
Figures 4-6 show the SEM micrographs of the relative sizes of the clay particles at X 500 magnification and the spectra depicting the peaks of the elements present. This analysis has confirmed that the clays contained high percentages of iron in form of iron oxide as was also observed in the XRF analysis (Table 1) and hence the need for their removal via leaching with the help of oxalic acid.

3.3 Transmission Electron Microscopy (TEM)



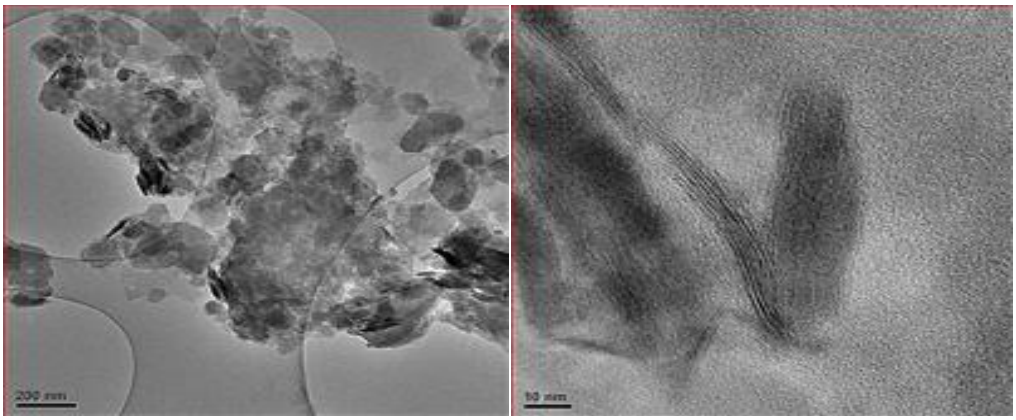
(a) Raw Clay before leaching (b) Clay after leaching

Figure 7: Transmission Electron Micrographs (TEM) of As-mined and TreatedIjapo Clay



(a) Raw Clay before leaching (b) Clay after leaching

Figure 8: Transmission Electron Micrographs (TEM) of As-mined and TreatedIre Ekiti Clay



(a) Raw Clay before leaching (b) Clay after leaching

Figure 9: Transmission Electron Micrographs (TEM) of As-mined and TreatedIlesha Clay

The micrographs show the distribution of the minerals present in them. The minerals occurred as agglomerates in the unprocessed clays but after undergoing the purification process, they became finely and uniformly distributed in the bulk. The uniform dispersion of the minerals in the processed clays enabled the oxalic acid to make direct contacts with virtually all the grains in the clays and hence the ease to remove the iron present in them.

3.4 X-ray Fluorescence (XRF)

Table 1. XRF Analysis of the raw and leached clays

Oxides	Ijapo Clay		Ire Ekiti Clay		Ilesha Clay	
	Raw	Leached	Raw	Leached	Raw	Reached
SiO_2	62.17	64.51	58.96	57.17	64.04	65.94
Al_2O_3	23.85	21.64	22.78	27.62	16.78	15.79
CaO	0.60	2.56	0.63	3.58	0.36	3.38
Fe_2O_3	6.76	3.15	4.95	0.96	6.94	3.59
MgO	0.73	0.27	0.81	1.12	0.63	0.37
K_2O	1.22	1.12	3.78	1.18	2.99	1.17
Na_2O	0.11	0.11	1.08	0.78	0.85	0.19
MnO	0.10	0.12	0.08	0.03	0.03	0.03
TiO_2	0.21	1.08	0.66	1.88	1.11	1.17
P_2O_5	0.07	0.07	0.05	0.05	0.04	0.03
Cr_2O_3	0.06	0.04	0.01	0.02	0.03	0.02
NiO	0.05	0.07	0.01	0.01	0.02	0.01
V_2O_5	0.06	0.09	0.01	0.02	0.02	0.02
ZrO_2	0.09	0.15	0.08	0.04	0.07	0.06
LOI	4.57	5.75	6.89	5.80	6.53	8.71
Total	100.65	100.73	100.78	100.26	100.44	100.48

For the three clays, the iron oxide contents were reduced after leaching; from 6.76 to 3.15 % for Ijapo clay; 4.95 to 0.96 % for Ire Ekiti clay and 6.94 to 3.59 % for Ilesha clay. These represent 53.40 %, 80.61 % and 48.27 % for Ijapo, Ire Ekiti and Ilesha clays respectively. It was also observed that there were reductions in the contents of deleterious oxides, such as K_2O and Na_2O after leaching, for the three clays. The total percentage of K, Na and Mg oxides altogether was virtually 2%, which is the limit recommended for insulating firebricks [15,16]. However, there were increases in the contents of refractory oxides such as CaO and Al_2O_3 in the clays because their relative presence has been affected by the reduction in the contents of the identified impurities (Fe_2O_3,K_2O, Na_2O and MgO). These increases are however, desirable for the improvement of the refractoriness of the clays.

3.5 XRD Quantitative Analysis

Table 2 shows the mineralogical analysis carried out to identify and determine the relative amounts of minerals contained in the clays before and after purification.

Table 2 XRD Quantitative Analysis of As-mined and Hydrometallurgically Treated Clays

% Weight of Clay Minerals before and after Leaching

Clay Minerals	Ijapo Clay		Ire Ekiti Clay		Ilesha Clay	
	Raw	Treated	Raw	Treated	Raw	Treated
Kaolinite	6.33	8.98	19.12	37.23	35.74	38.39
Muscovite/Illite	2.96	5.40	16.12	28.01	13.63	22.69
Quartz	43.82	36.70	24.40	15.44	40.42	32.13
Microcline	29.45	35.25	25.14	8.95	5.16	2.32
Plagioclase Albite	17.44	13.65	15.22	10.86	5.05	4.47
TOTAL	100.00	99.98	100.00	100.49	100.00	100.00

Muscovite/illite and kaolinite levels increased as expected in all the clays after purification, but the increase was more noticeable in Ire Ekiti clay just as the expected reduction rate in quartz level was more pronounced in it. Hence, on the basis of the quality of the raw clay, the effectiveness of the leaching process and presence of the most desired clay minerals, Ire Ekiti clay was found to be the most suitable of all the three clays. Consequently, it was selected for the production and testing for insulating qualities after leaching.

3.6 Permanent Linear Change (PLC)

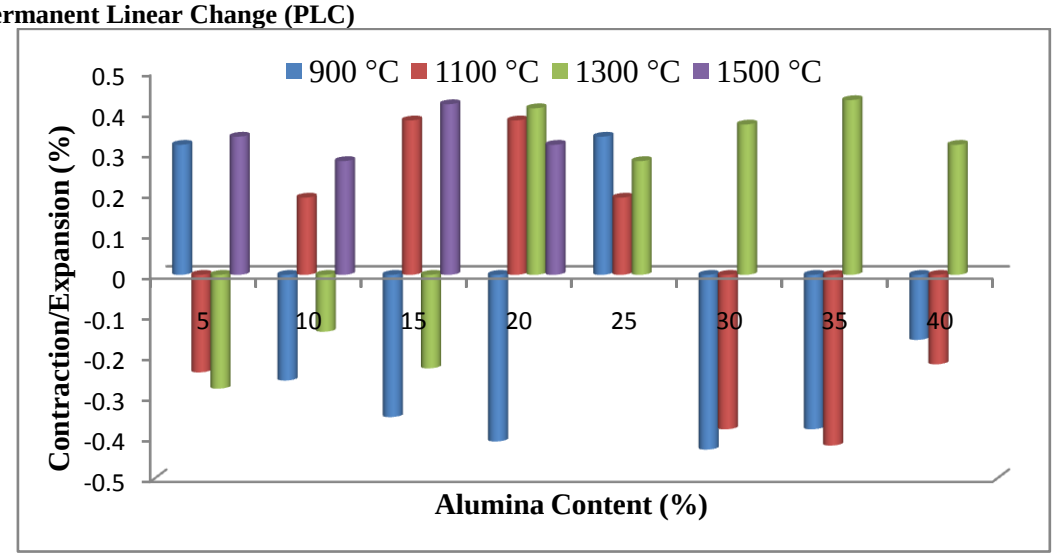


Figure 10: Permanent Linear Changes of TreatedIre Ekiti clay plus alumina cement at different firing Temperatures

It was observed that the firebricks underwent linear contractions for firing temperatures of 900 ºC, 1100 ºC and 1300 ºC for low additions of alumina. For alumina contents between 20 and 30% the firebricks suffered permanent linear expansion after which the bricks suffered permanent linear contraction again. This is indicative of variations in the clay-alumina reactions at different alumina contents. When fired at 1500 ºC, the bricks suffered permanent linear expansion for alumina additions up to 20 %, beyond which the bricks became dimensionally unstable and crumbled under its own weight. This accounted for the reason samples with 25 % alumina and above did not feature on the graph.

3.7Modulus of Rupture (MOR)

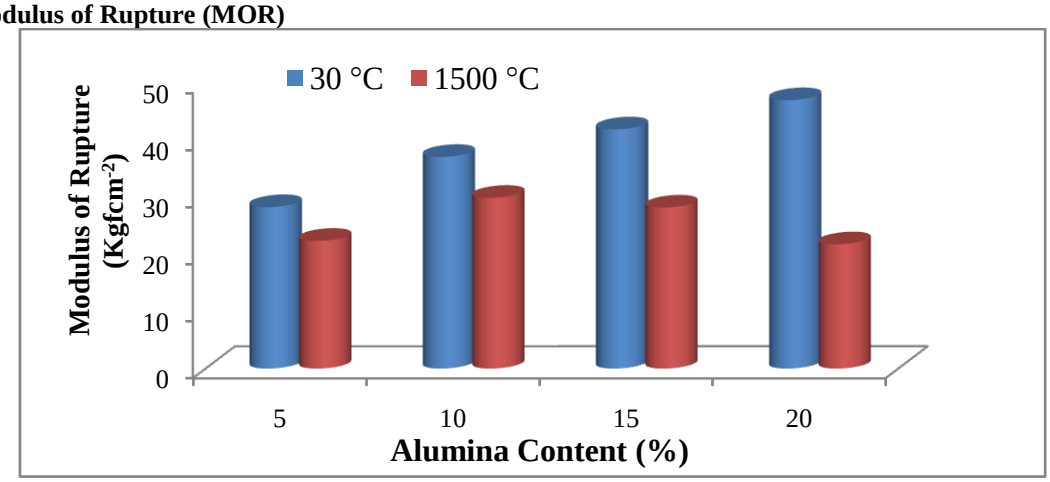


Figure 11: Variation of Modulus of Rupture of TreatedIre Ekiti clay with alumina Contents at room temperature (30^{o}C) and 1500 ^{o}C

The MOR was much lower when tested at 1500 ^{o}C than at the room temperature (30^{o}C). The values increased progressively with the quantity of alumina in the cold state while it only increased to the maximum at 10 % alumina and dropped again when tested at 1500 ºC. The trend was due to the fact that the liquid so formed when the samples were first heated and allowed to cool had solidified to form glass which further strengthened the samples. On the other hand, when the samples were rupture tested at the elevated temperature of 1500 °C, the samples were still in the molten state and thus the strength was comparatively lower than when it had solidified to form glass. However, the MOR attained maximum at 10 % alumina because the liquid phase formed when fired was adequately matched with the alumina present to form a solid mass and hence the relatively higher strength than at 15 % and 20 % alumina where the liquid phase was predominant.

3.8Apparent Porosity

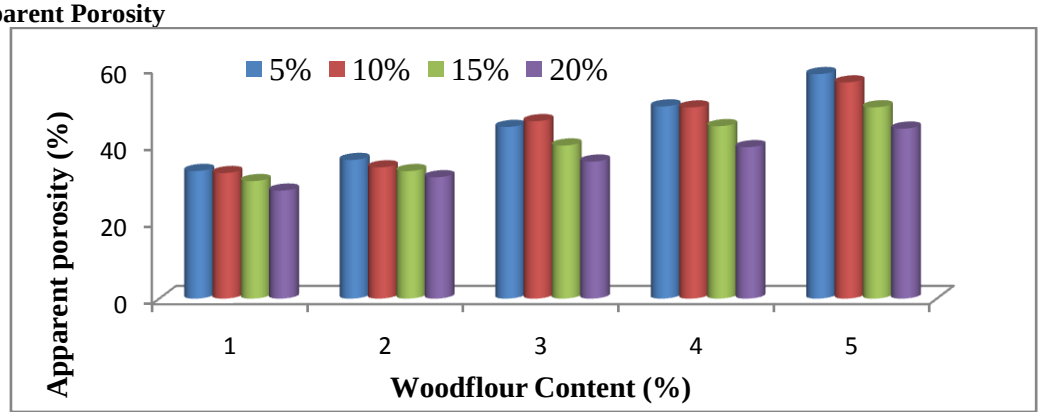


Figure 12: Variation of Apparent porosities of TreatedIre Ekiti clay plus alumina cement with wood flour

The apparent porosity increased as the percentage of woodflour increased at all levels of alumina content because the woodflour burnt off at the elevated temperature of 1500 ºC. The more the woodflour added, the more the pores created. Despite this trend, the porosity still reduced with alumina at each woodflour content. The reduction is attributable to the increased binding effect of alumina in the samples, which binds the grains together, thereby reducing the interparticle distances and hence the reduction in the porosity. The results show that 3-5 % sawdust exhibited the desired expectations; ≥ 45 % porosity [17]. High strength, however, is incompatible with high porosity because the larger and more numerous the pores, the thinner the enclosing wall of solid material and the lower the strength [18]. Sample with 10 % alumina and 3 % sawdust was therefore chosen as the most promising of the samples because it possesses apparent porosity of 46.22 %.

IV. Conclusion

1. The various characterization techniques showed consistency in the revelations of the relative constituents of the clays,
2. Ire Ekiti clay, however, revealed the best compliance to purification as clearly shown by the results of the various characterization techniques adopted.
3. Purified Ire Ekiti clay containing 10 % alumina cement and 3 % woodflour exhibited a good combination of the required properties of a good insulating material for high temperature applications.
4. Ire Ekiti clay is therefore, recommended for use in thermal insulation because of the relative ease of removing iron bearing minerals from the clay.

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