Hydrometallurgical Purification of Some Clay Deposits for High Temperature Applications

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ABSTRACT

The characterization of five different Nigerian clay deposits has been carried out by employing three different characterization techniques (X-ray Diffraction, X-ray Fluorescence and Scanning Electron Microscopy/EDX). The clays obtained from the various deposits were carefully prepared for the analyses and the results obtained were compared to confirm the consistency and reliability of the different methods employed. The results revealed the various desirable (S_iO_2 and Al_2O_3) and deleterious (Fe_3O_4, K_2O, MgO, MnO and Na_2O) elements and compounds contained in the clay samples in the various proportions and the appropriate purification technique required for preparing the clays for high temperature applications. Consequent upon the identification of the deleterious impurities, oxalic acid at different concentrations was used to leach the impurities out of the various clays. However, three out of the five deposits were chosen for purification because they possess the least quantities of the most deleterious (Fe_2O_3) of the impurities.

Keywords: *Hydrometallurgy, Purification, High Temperature, Clay and Characterization.*

1. INTRODUCTION

Refractories are materials that can withstand high temperature and chemical attack in the severe conditions of working [1,2]. They are thermal insulators and therefore used for making furnace linings, kilns, nozzles for pouring molten metal, heat exchangers and driers, to mention a few [3,4]. Applications in furnaces include anything from primary metal melting, through to heat treatment, glass production and processing, ceramic component manufacture, many forms of chemical processing and testing [5,6].

The term "clay" refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired [7]. Although clay usually contains phyllosilicates, it may contain other materials that impart plasticity and harden when dried or fired.

Earlier works on various Nigerian refractory clay deposits have shown many of them to be unsuitable for refractory works 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]. The unsuitability of the local clay deposits for refractory works in the as-mined states has therefore prompted the need for this work, which is principally aimed at characterizing and subsequently purifying them in readiness for the production of materials for high temperature applications.

2. MATERIALS AND METHOD

Research Materials
- Clays from:

Ifon in Ondo State (sample A)

Igbara-odo in Ekiti State, (B)

Ipetumodu in Osun State (C)

Isan-Ekiti in Ekiti State (D)

Iseyin in Oyo State, (E)

Five Clay samples from five different clay deposits in different parts of the South – Western part of Nigeria were prepared for analysis. The clays were those from Iseyin in Oyo State, Ipetumodu in Osun State, Ifon in Ondo State, Igbara-Odo and Isan in Ekiti State. They are coded as listed above for ease of identification. A combination of X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM) analyses were carried out to investigate the mineralogical composition of the five prepared samples (A-E) Hydrometallurgical purification was then employed to remove the identified impurities (Fe_2O_3, MnO, MgO, Na_2O, CaO) from the five samples.

3. RESULTS AND DISCUSSION

3.1 XRF Elemental Analysis Studies

The results of the X-ray fluorescence semi-quantitative analysis of the elements in the clay samples are as shown in Table 1.

The results show that sample A contains the highest amount of silica by mass (63.35%), followed by sample E with 62.29% and with sample D having the least (54.67%). Sample B contains the highest amount of Alumina (25.73%) followed by sample C with 25.03% while sample A contains the least with 22.42%. sample D indicated the highest amount of Ferric oxide (10.408%), closely followed by sample B with 9.226% while sample A contains the least with just 6.109%. sample B has the greatest quantity of 2.94% by mass of potassium oxide, followed by sample A with 2.878% while sample C contains the least amount of just 1.259%. So also, sample D contains the highest amount of magnesium oxide (2.401%) followed by sample A with 1.351% while sample C contains the least with just 0.91%.

As clearly indicated in Table 1, all other minerals present are in such negligible proportion that their presence would not constitute threats to the performances of the clay as refractory materials.

Table 1: XRF semi-quantitative analysis of the elements

Element	Compound		Sample A	Sample B	Sample C	Sample D	Sample E
Al	Al_2O_3	(mass %)	22.42	25.737	25.03	23.98	22.729
Si	SiO_2	(mass %)	63.35	56.636	59.482	54.657	62.292
Fe	Fe_2O_3	(mass %)	6.109	9.226	8.652	10.408	7.266
K	K_2O	(mass %)	2.878	2.94	1.259	2.513	1.36
Mg	MgO	(mass %)	1.351	1.166	0.91	2.401	0.985
Ba	Ba	(mass %)	0.092	0.102	0.083	0.08	0.065
Ca	CaO	(mass %)	0.689	0.911	0.763	0.843	0.541
Cl	Cl	(mass %)	----	0.016	0.015	0.028	0.026
Co	Co	(mass %)	----	0.025	0.017	0.08	0.034

Cr	Cr$_2$O$_3$	(mass %)	0.046	0.05	0.045	0.036	0.043
Cu	Cu	(mass %)	0.021	0.034	0.026	0.137	0.046
Mn	MnO	(mass %)	0.117	---	0.045	0.109	0.05
Na	Na$_2$O	(mass %)	0.789	1.229	0.372	0.604	0.259
Ni	Ni	(mass %)	0.064	0.042	0.078	0.061	0.074
P	P$_2$O$_5$	(mass %)	0.109	0.051	0.047	0.049	0.058
S	SO$_3$	(mass %)	0.047	0.026	0.028	0.016	0.123
Sr	Sr	(mass %)	0.019	----	0.019	0.015	0.008
Ti	TiO$_2$	(mass %)	0.923	0.895	1.512	1.577	1.046
Zr	Zr	(mass %)	0.045	0.02	0.103	0.028	0.056
Total		(mass %)	99.1	99.07	98.526	97.7	97.1
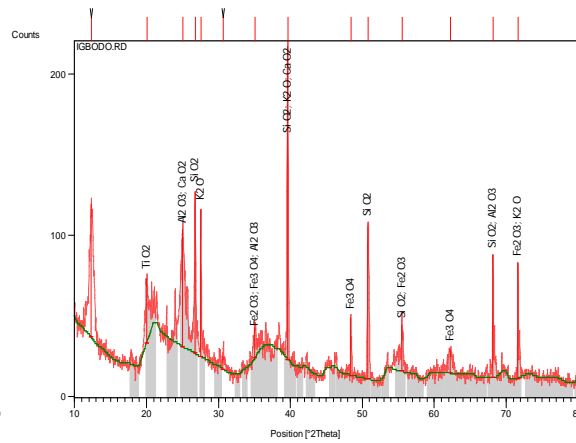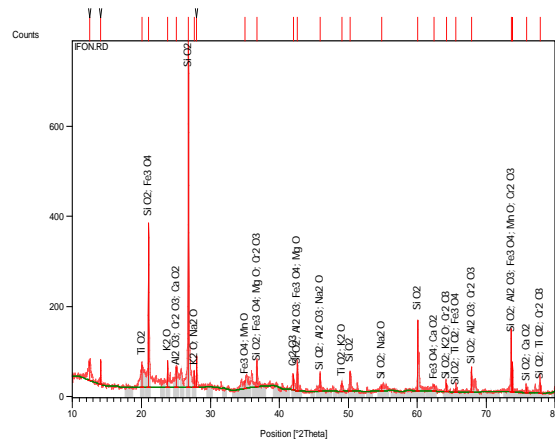
Figure 1: X-ray diffraction pattern of Sample A.   Figure 2: X-ray diffraction pattern of sample B
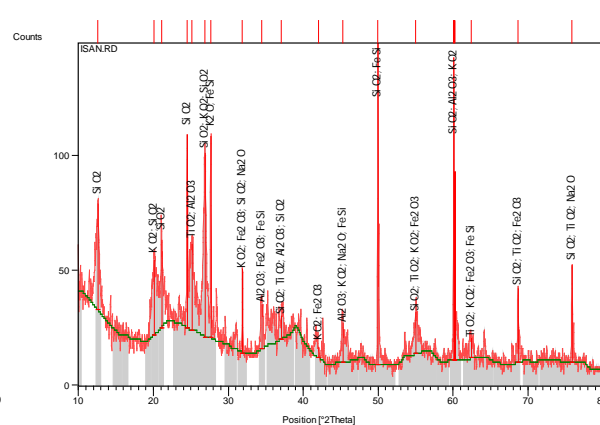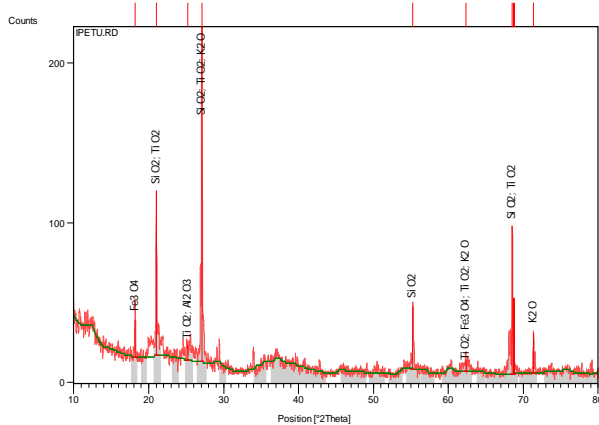
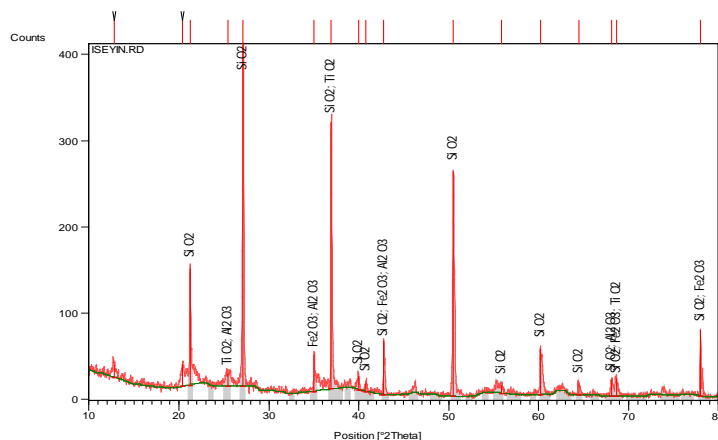Figure 3: X-ray diffraction pattern of sample C.   Figure 4: X-ray diffraction pattern of sample D

Figure 5: X-ray diffraction pattern of sample E

3.2 XRD Analysis

The diffractograms (Figures 1-5) show the X-ray diffraction pattern of the as-received five clay samples. Careful investigation reveals that the samples are composed essentially of S_1O_2, Al_2O_3, Fe_3O_4 and to very limited extent of K_2O, MnO, Na_2O and CaO. Some other oxides are also present but in very negligible proportions.
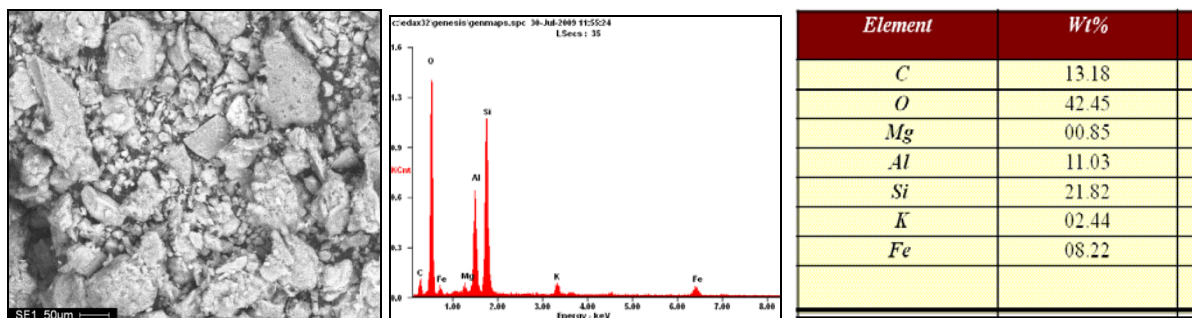

Element	Wt%	
C	13.18	
O	42.45	
Mg	00.85	
Al	11.03	
Si	21.82	
K	02.44	
Fe	08.22	

Figure 6: Typical SEM/EDX Micrographs of Sample A Showing the Morphology of the Clay and its Chemical Composition

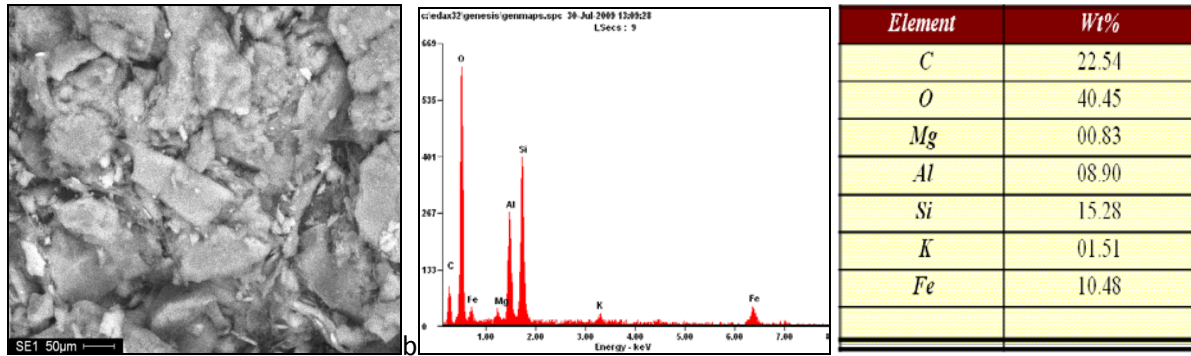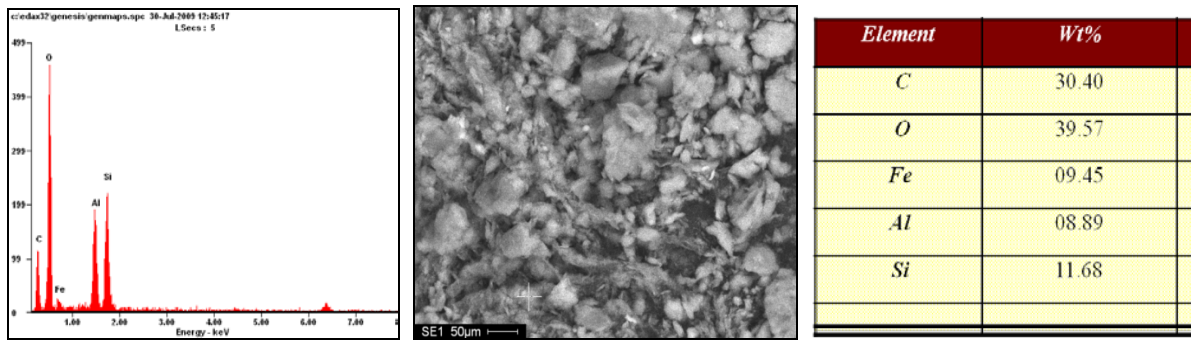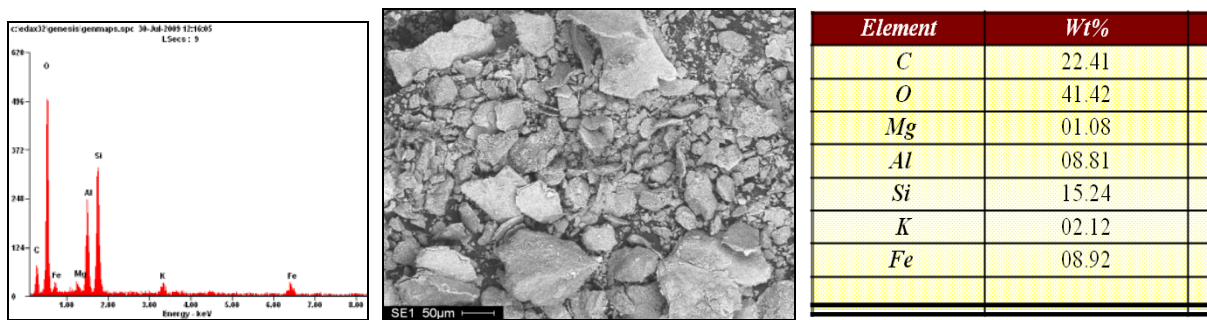| Element	Wt%
C	22.54
O	40.45
Mg	00.83
Al	08.90
Si	15.28
K	01.51
Fe	10.48

Figure 7: Typical SEM/EDX Micrographs of Sample B Showing the Morphology of the Clay and its Chemical Composition

Element	Wt%
C	30.40
O	39.57
Fe	09.45
Al	08.89
Si	11.68

Figure 8: Typical SEM/EDX Micrographs of Sample C Showing the Morphology of the Clay and its Chemical Composition

Element	Wt%
C	22.41
O	41.42
Mg	01.08
Al	08.81
Si	15.24
K	02.12
Fe	08.92

Figure 9: Typical SEM/EDX Micrographs of Sample D Showing the Morphology of the Clay and its Chemical Composition

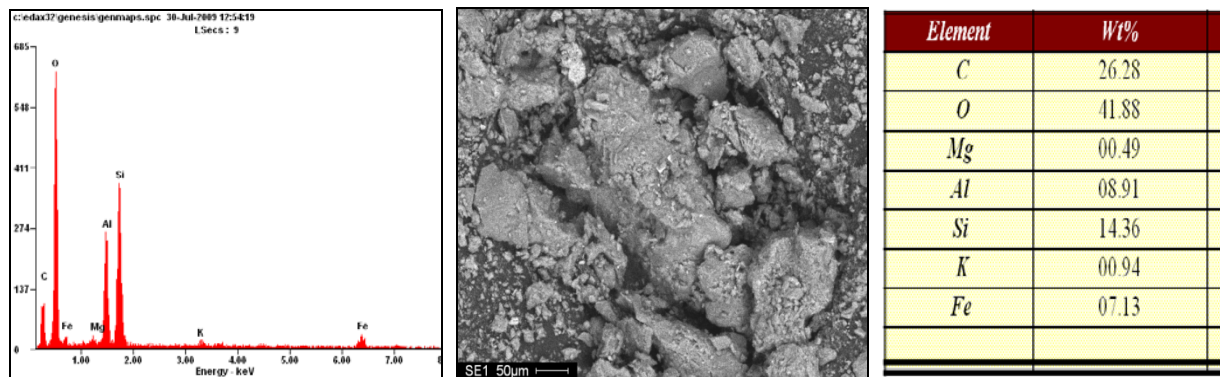| Element	Wt%
C	26.28
O	41.88
Mg	00.49
Al	08.91
Si	14.36
K	00.94
Fe	07.13

Figure 10: Typical SEM/EDX Micrographs of Sample E Showing the Morphology of the Clay and its Chemical Composition

3.3 Scanning Electron Microscopy (SEM)

Figures 6-10 show the different morphologies of the clays and their chemical compositions at both general surfaces and selected areas. The chemical compositions of the clays as revealed by Energy–Dispersive X-ray (EDX) analysis indicated very reasonable similarities with those of XRD and XRF.
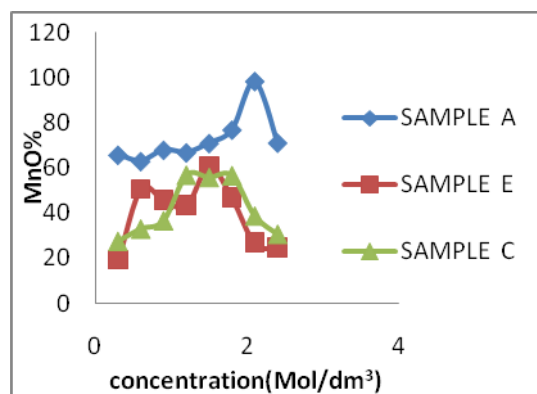
Figure 11: Variation of Manganese Oxide Removed
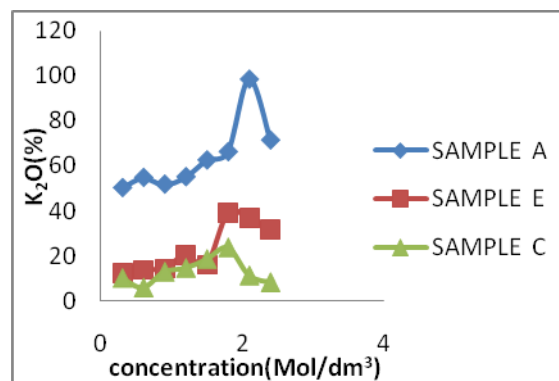

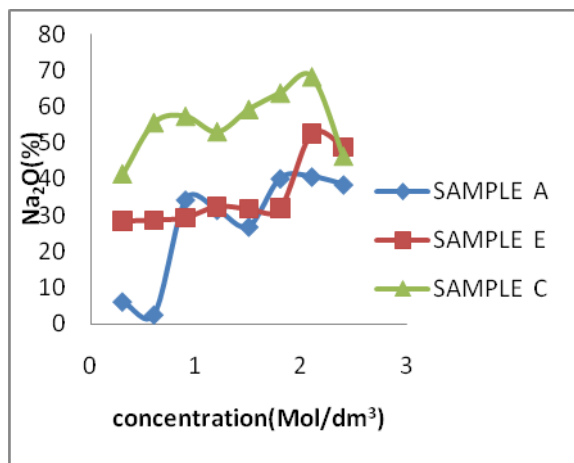Figure 12: Variation of Potassium Oxide Removed

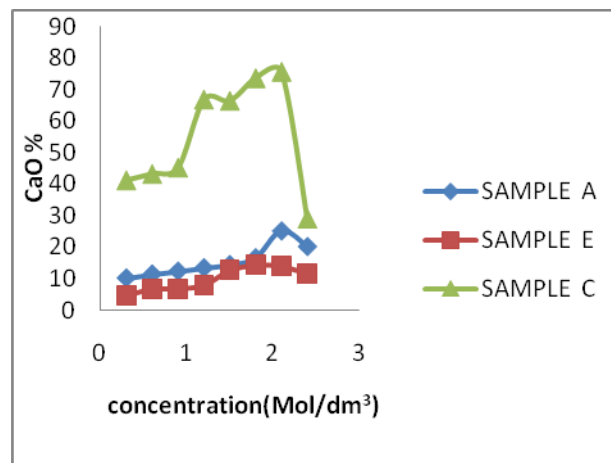Figure 13: Variation of Sodium Oxide Removed

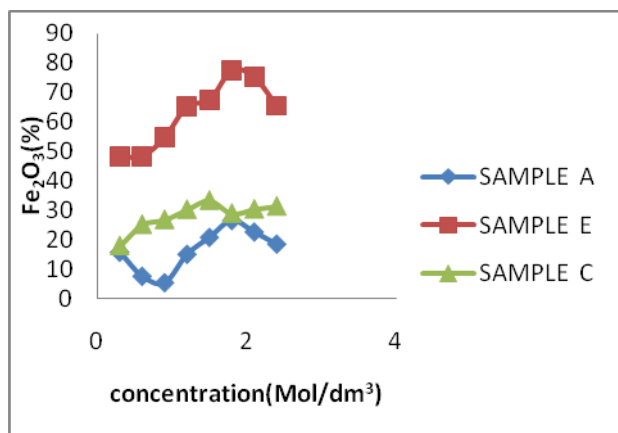Figure 14: Variation of Calcium Oxide Removed

Figure 15: Variation of Iron oxide Removed

3.4 Hydrometallurgical Purification

Consequent upon the identification of the deleterious impurities as revealed by the various characterization techniques adopted, the removal was embarked upon with the use of different concentrations of oxalic acid (0.3, 0.6, 0.9, 1.2, 1.5, 1.8, 2.1 and 2.4 mol/dm^3) at room temperature. The results as presented in figures 11 to15 clearly show that the purification with the use of oxalic acid is an effective one, with the range of 1.8 -2.1 mol/dm^3 of oxalic acid being the most effective concentrations for purification.

4. CONCLUSION

The combination of the three characterization techniques adopted in this study (XRD, XRF & SEM/EDX) showed consistency in the revelation of the quantities of the desired elements (Al_2O_3 and SiO_2) and the deleterious impurities (Fe_2O_3, K_2O, MgO, Na_2O, CaO and MnO) contained in the samples. The application of oxalic acid in the purification process also showed a very reasonable degree of effectiveness, with the range 1.8-2.1 mol/dm^3 of the acid being the most effective concentrations for purification. The clays after purification have the potential for application in the production of acidic refractories.

ACKNOWLEDGEMENT

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