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PRODUCTION AND CHARACTERIZATION OF CLAY BONDED CARBON REFRACTORY FROM CARBONIZED PALM KERNEL SHELL

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Abstract: *The effects of varied contents of clay on the mechanical properties of clay bonded carbon refractory samples produced from Ifon clay and carbonized palm kernel shell was investigated. The physical, mechanical and morphological characterizations of the samples were carried out following American Society for Testing and Materials (ASTM) stipulated standards. The clay bonded carbon refractory samples were produced by mixing respectively 40, 50 and 60 weight percents processed clay obtained from Ifon, Ondo State, Nigeria and carbonized palm kernel shell. Each mixture was uniaxially compressed into standard samples dimension and then fired in the furnace at 950°C. The characterized/investigated properties were bulk density, cold crushing strength, porosity, water adsorption, young's modulus and absorbed energy. Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy using back scattered secondary imaging were used to determine the chemical compositions, size, and morphology of the produced clay bonded carbon refractory. The result shows that the compositions of Ifon clay are of kaolinite, microcline, muscovite, plagioclase and quartz. The result also reveal that the apparent porosity and water adsorption increases with increase in carbonized palm kernel shell content while other properties such as bulk density, cold crushing strength, young's modulus and absorbed energy decreases with increase in the carbonized palm kernel shell content. It was however concluded that the composite grade containing 40 wt % carbonized palm kernel shell and 60% ifon clay, had the best combination of mechanical properties of all the composites produced.*

Keywords: *clay bonded carbon refractory, composite, palm kernel shell*

1. INTRODUCTION

Refractory materials are non-metallic materials that provide linings for high-temperature furnaces and other processing units. Refractories unusual withstand physical wear, corrosion by chemical, high melting temperatures and maintain their structural properties at very high temperatures [1-3]. Refractories are employed in great quantities in the metallurgical, glassmaking, and ceramics industries, where they are formed into a variety of shapes to line the interiors of furnaces, kilns, and other devices that process materials at very high temperatures [4, 5]. Refractory materials are very useful and play very crucial roles in the industrial development of any nation. The Nigerian metallurgical industries are struggling today because of many factors which include short supply of refractory materials. It was however reported that Ajaokuta Steel Complex requires about 43,503 tonnes per year of fireclay refractories for its operations; and these refractories are sourced abroad [6,7]. Despite having extensive clay mineral deposits in Nigeria, Nigeria continues to depend on external sources of refractory materials for many of its industries [8].

The characteristic properties of a refractory are a function of both raw material base and the method of production used for the refractory product. Refractory manufacturing involves four processes: raw material processing, forming, firing and final processing [9]. In this research, clay bonded carbon refractory is considered and produced by adding processed clay with carbonized palm kernel shell and firing to a sufficient temperature to vitrify the clay and to produce a bond with the carbonized palm kernel shell.

Carbon and graphite in refractories produces extraordinary properties for special applications. Carbon is desirable element for refractory use because it is not wetted by most molten metals and slags; it has excellent thermal shock resistance; good strength and susceptibility to oxidation [10]. However, its use is limited to applications which are either strongly reducing or where the oxygen content of the atmosphere at a given operating temperature is low enough to prevent appreciable combustion of the carbon.

Many researchers have reported on their various successes in the production of activated carbon using agro-waste materials and by products such as Fluted Pumpkin Stem Waste (Telfairia occidentalis Hook F) [11], macadamia nutshell [12], coconut shell [13] and rice husk [14], Palm kernel shell and coconut shell [15]. Activated carbon is an organic material that has an essentially graphitic structure. The main features common to all activated carbon are; graphite like planes which show varying degrees of disorientation

But there have been little information on the use of these carbonaceous materials gotten from the conversion of these agro-waste materials in the production of refractory materials for industrial use. The current work is aimed at this the possibility of utilizing these vast available material (palm kernel shell) in the fabrication of refractory materials. In view of all these facts, there is therefore every need to produce, characterize, evaluate and improve the refractory properties of the Ifon clay deposit in Ondo State Nigeria with the addition of carbonized palm kernel shell.

2. MATERIALS AND METHODS

2.1. Materials

The materials utilized in this research work are Ifon clay and Carbonized palm kernel shell. The Ifon clay was collected from Ifon (an area fond to be rich in fireclay), Ose Local Government Area of Ondo State (latitude 7^{O} 52` N and longititude $7^{O}$ 28` 60 E). The clay lumps were crushed, grounded and sieved.

2.2. Clay Processing Procedure

This clay samples as obtained was soaked in water for three days to dissolve the clay and at the same time to form slurry. The resulting slurries were then sieved to remove dirt and other foreign substances using a sieve. These were then allowed to settle down for seven days after which the floating clear liquids were decanted. The settled fine clays is then poured into Plaster of Paris (P.O.P) moulds and left undisturbed for three days in other to allow the liquid present to drain out completely. The resulting plastic clay mass were sun dried and subsequently dried in a laboratory oven at 110^{o}C for 24 hours to remove moisture content completely.

The resulting dried clay samples were milled at 300 rev/ min for 4 hour to an average particle size of about 300μm. The carbonized palm kernel shell was produced as described by Ekpete and Horsfall [11], with the exception that the carbonization took place at 700^{o}C. A mixture of clay and carbonized palm kernel shell was made using ball-mill for six hours using respectively 40, 50 and 60 weight percents of Ifon clay in each mix. Each mixture was made thoroughly with a little addition of water to induce some plasticity. The samples were then compressed uniaxially inside a standard stainless steel die. The compressed samples were placed in a ceramic crucible, properly sealed to limit the amount of air that will be in contact with the samples during firing. The crucibles containing the samples were placed in a muffle furnace and then fired (sintered) at 950^{o}C, held at the temperature for 1hr. The percentage weights ratio of the mix is presented in Table 1:

Table 1. Percentage mass of representative samples

Composition	Carbonized palm kernel shell (%)	Ifon clay (%)
A	40	60
B	50	50
C	60	40

2.3. Apparent Porosity

Produced clay bonded carbon refractory samples were dried for 12 hours at 110°C. The weight of the dried samples were taken and recorded as D. The samples were immersed in water for 6 hours to soak and weighed while been suspended in air. The weight will be recorded as W. Finally, the specimen will be weighed when immerse in water. This will be recorded as S. The apparent porosity will then be calculated from the expression:

$$p = \frac{(W - D)}{(W - S)} \times 100\%$$

2.4. Cold Compression Strength

Cold compression strength test was used to determine the compression strength to failure of each sample, an indication of its probable performance under load. The standard samples were dried in an oven at a temperature of 110°C, and then allowed to cool. The cold compression strength test was performed on INSTRON 1195 at a fixed crosshead speed of 10mm min^{-1}. Samples were prepared according to ASTM D412 (ASTM D412 1983) and tensile strength of standard and conditioned samples can be calculated from the equation:

$$CCS = \frac{\text{Load to Fracture}}{\text{Surface Area of Sample}}$$

2.5. Water Absorption Test

Water absorption tests were carried out following standard procedures. Samples of each composite grade were oven dried before weighing and the weights recorded were reported as the initial weight of the composites. The samples were then placed in distilled water maintained at room temperature (25^0C) and at time intervals of 24h, the samples were removed from the water, cleaned using a dry cloth and weighed. The weight measurements were taken periodically at time intervals of 24h. The amount of water absorbed by the composites (in percentage) was calculated using the equation:

$$W = W_T - W_0/W_0$$

2.6. Bulk Density

The test specimens were dried at 110°C for 12 hours to ensure total water loss. The dried weights were measured and recorded. Samples were allowed to cool and immersed in a beaker of water. Bubbles were observed as the pores in the specimens were filled with water. Their soak weights were measured and recorded. Bulk densities of the samples were calculated using the formula:

$$bulk\ density = \frac{D}{(W - S)}$$

Where : D = Weight of dried specimen, S = Weight of dry specimen suspended in water, and W = Weight of soaked specimen suspended in air

2.7. Qualitative and Quantitative (XRD)

The samples were prepared for XRD analysis using a back loading preparation method. The samples were analyzed using a PANalyticalX'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-Ka radiation. The phases obtained were identified using X'PertHighscore plus software. Graphical representations of the qualitative result will then follow. The relative phase amounts in weight % were estimated using the Rietveld method (Autoquan Program). Amorphous phases, present were not taken into consideration in the quantification.

2.8. Scanning Electron Microscopy

Morphology and microanalysis of the clay and composite samples were determined using ultra-high resolution field emission scanning electron microscope (UHR-FEGSEM) equipped with energy dispersive spectroscopy (EDS). The pulverize clay samples were graphite coated. The sintered samples were studied using ultra-high resolution field emission scanning electron microscope (UHR-FEGSEM) equipped with energy dispersive spectroscopy (EDX). Particle images which are obtained with a secondary electron detector.

2.9. Chemical Analysis

The major elements were determined by X-ray fluorescence with an ARL® 9800 XP spectrometer. The pulverized samples were mixed with lithium tetra borate for chemical analysis. The ignition loss was measured by calcinations at 1000 °C.

3. RESULTS AND DISCUSSIONS

Figures 1 and 2 respectively shows the XRD result and SEM/EDX analysis of the raw clay sample. Table 2 also shows the XRD analysis results of the raw clay sample. These show the various phases present in the raw clay sample. It can be seen from Table 1 that the overall feldspar contents of the raw clay samples are high (30.90% microcline and 18.22% Plagioclase Albite).

Table 2: XRD result of the Ifon clay sample showing the quantity of phases

Phases identified	Weight%
Kaolinite	5.63
Microcline	30.90
Muscovite/illite	3.81
Plagioclase albite	18.22
Quartz	41.42

It has been noted that feldspars favour liquid phase formation and densification at low temperature; this will disqualify the utilization of the clay in *refractory (high temperature) applications except if subjected to serious purification process to reduce or eliminate the feldspar content and the fusion point of the fireclay increases [16, 17].*

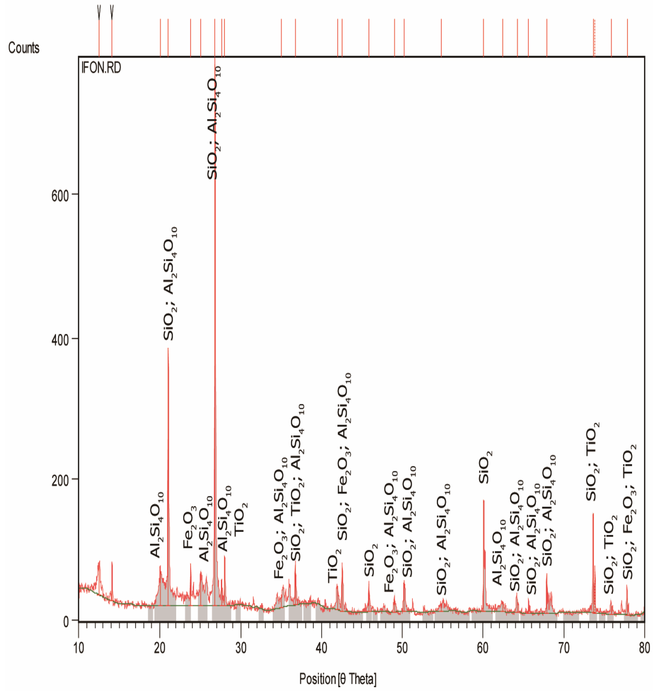
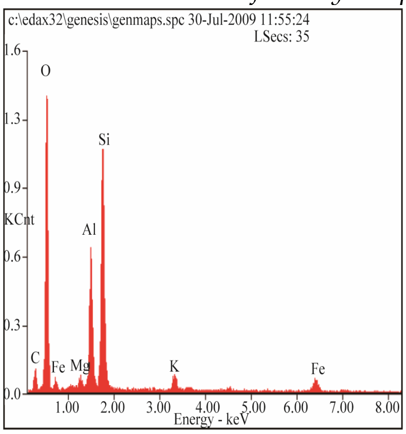


Figure 1: X-ray diffraction pattern (phase analysis) of the Ifon clay sample.



Element	wt%
O	42.45
Mg	00.85
Al	11.03
Si	21.82
K	02.44
Fe	08.22

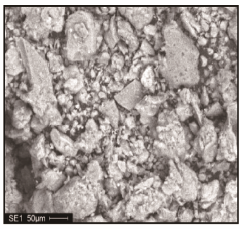


Figure 2: Typical SEM/EDS of Ifon clay sample; showing the morphology of the minerals and its chemical composition.

3.2. Effects on the mechanical properties

The apparent porosity of the clay bonded carbon ceramic samples are presented in Figure 3. It is observed that the porosity of the sample increases with the increase in carbonized palm kernel shell content from 5.15 % at 40 % carbon to a maximum of 18.78 at 60 % carbon addition. It has been observed that as the graphitic content of carbon based refractory increases, the density of the refractory decreases. This result is primarily due to the fact that the morphology of the graphite as compared to the other refractory materials. The graphite materials, which are used in refractories, are commonly of a flaky structure; therefore, these flakes do not lend themselves to the same particle packing phenomena as do granular particles. The flaky morphology gives rise to high porosity; some of these pores are filled up by the clay particles. As the percentage content of the carbonized palm kernel shell increased, the percentage content of clay in the sample reduced, which means less clay particles are available to fill the pores between the flakes of carbon, hence the increased porosity with increased percentage content of the carbonized palm kernel shell.

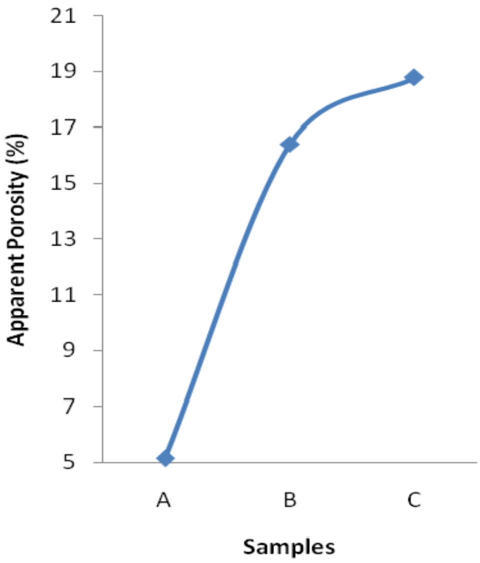


Figure 3: Effect of carbonized palm kernel shell on the apparent porosity of the samples

Moreover, one of the authors has earlier reported that the clay deposit used as binder in this work contains feldspar as it is observed in Table 2. These feldspar content is known to favour low temperature liquid phase sintering [18]. As the clay content increase (reduced content of carbonized palm kernel shell), more feldspathic clay particles are available to form more liquid phase during sintering at the sintering temperature. This liquid phase then flows into the pores filling up some of the pores.

From Figure 4, show the effects increase in the amount of carbonized palm kernel shell on the bulk density of the test samples. It is observed that there is a general decrease in the density of the samples with increase in the weight percent of the carbonized palm kernel shell from 40 to 60 wt% in the composites. The decrease in density with *increase in carbonized palm kernel shell content is obviously due to the lower density of the carbonized palm kernel shell in comparison with the raw clay samples.*

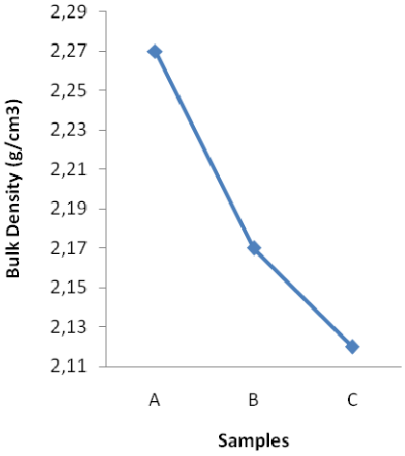


Figure 4: Effect of carbonized palm kernel shell on the Bulk density of the sample

From Figure 5, it is also observed that the cold crushing strength of the samples reduced with increased percentage carbonized palm kernel shell. This is because the increased percentage carbonized palm kernel shell leads to reduced matter content of the sample; less matter are available to bear the applied load. A brick of high porosity will have lower load bearing capacity than one of the same material with lower porosity, since there is less material in the brick to carry the load in the former case. Porous bricks are lighter and therefore unlikely to carry heavy load [18, 19].

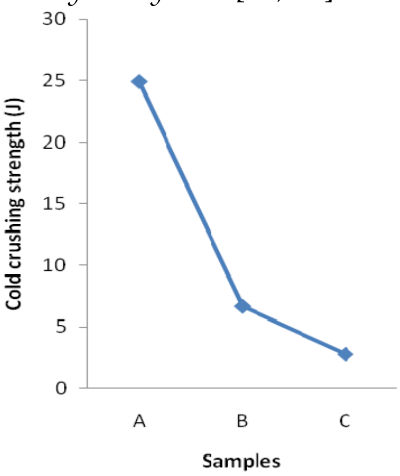


Figure 5: Effect of carbonized palm kernel shell on the cold crushing strength of the samples

Young's modulus which is a measure of a material's rigidity is presented in Figure 6. It is observed that the young's modulus decreases linearly with increase in weight percent of carbonized palm kernel shell. The curve shows that at 40 wt% carbonized palm kernel shell, young's modulus was at an initial value of 19103 N/mm², and thus decreases linearly at 50 wt% clay and 60 wt% carbonized palm kernel shell to a value of 3321.3 N/mm² and 2875.1 N/mm² respectively. This could be attributed to increase in the amount of open porosity in the sample which acts as 'notch' which is a stress (both mechanical and thermal) concentrator [20]

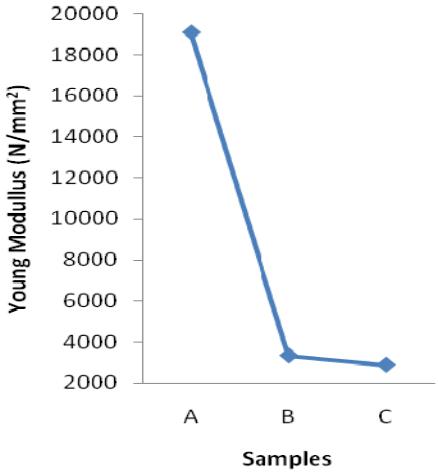


Figure 6: Effect of carbonized palm kernel shell on the young's modulus of the sample

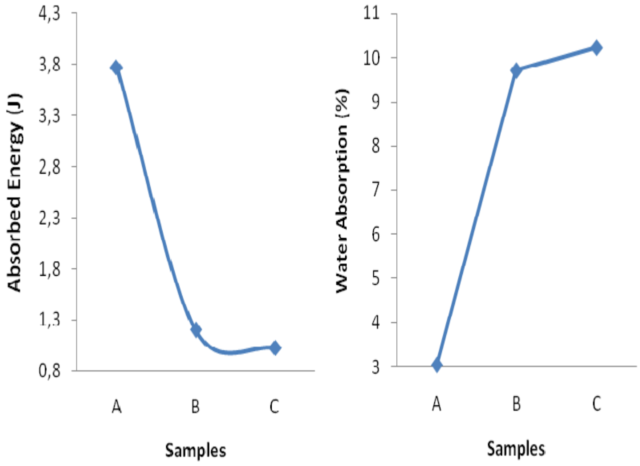


Figure 7: Effect of carbonized palm kernel shell on the (a) absorbed energy and (b) Water adsorption of the samples of the samples

From Figure 7a, it can be observed that the absorbed energy of the test sample decreases with increase in weight percent of carbonized palm kernel shell from 3.772 J at 40 wt% carbonized palm kernel shell to a minimum of 1.0294 J at 60 wt% carbonized palm kernel shell addition. The decrease observed in absorbed energy can be allotted to the increase in porosity in the samples. Thus, according to [21], the capacity of a porous

material in energy absorption can largely be characterized by its plateau strength and porosity.
Fig. 7b shows clearly that the amount of water absorbed by the composites increases with the increase in the carbonized palm kernel shell content of the samples. This suggests that the carbonized palm kernel shell is more hydrophilic in comparison with the raw clay sample. In adsorption, molecular attractions known as van der Waals forces play an active part as well as carbon being a porous adsorbent. The primary factors influencing adsorption are adsorbent characteristics, such as the size of interior surface area, pore structure, chemical properties.

3.3. SEM/EDS of the Carbon Bonded Refractory

The SEM/EDS microstructures of the carbon bonded clay composites are shown in Figures 8-10. Morphological analysis using SEM clearly show difference in the morphology of the raw clay sample (Figures 2 & 3) and its composites (Figures 8-10) created by the use of activated carbon.

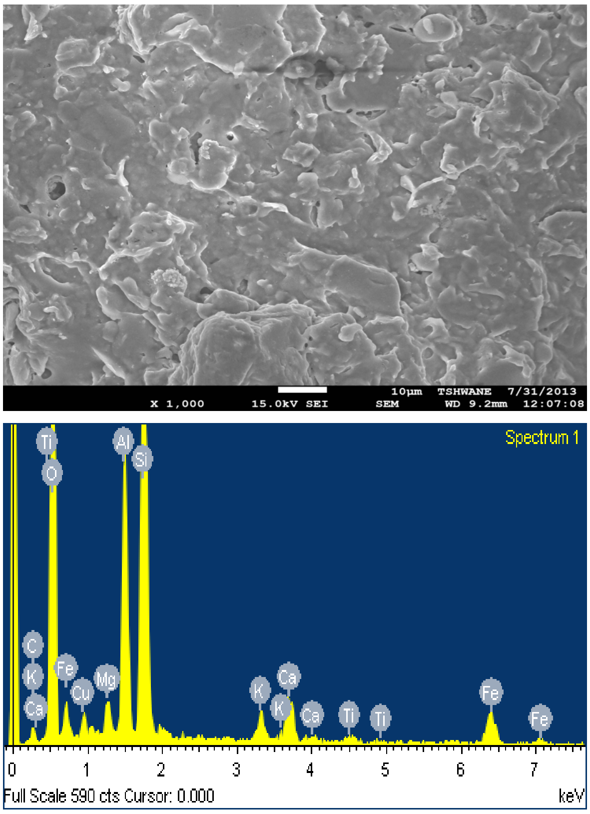


Figure 8: SEM/EDS Microstructure of the 40 % carbonized palm kernel shell addition

The microstructure clearly shows that when the carbonized palm kernel shell particle was added to the raw clay samples, morphological changes in the structure took place. The microstructure also reveals that the size and shape of the particles vary; however, they consist of porous irregular shape particles.

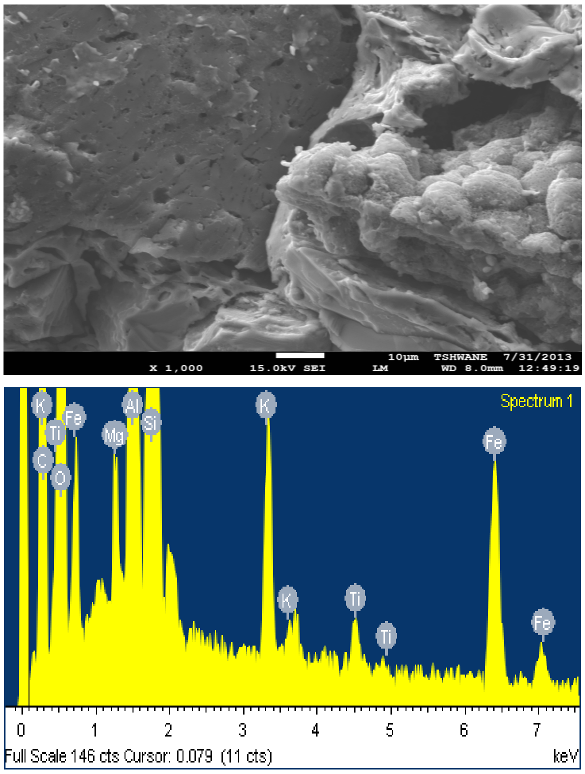


Figure 9: SEM/EDS Microstructure of the 50 % carbonized palm kernel shell addition

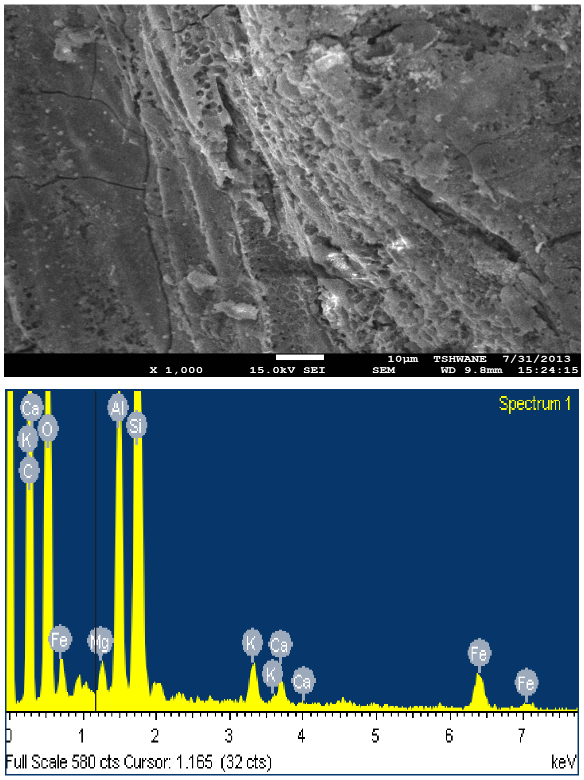


Figure 10: SEM/EDX Microstructure of the 60 % carbonized palm kernel shell addition

The EDS of the composite particles reveals that the particles contain Ca, Si, O, Mg, Al, Fe, P with the presence of C. The carbon presence is due to the carbonization process. These elements confirm that, carbonized palm kernel shell particles consists of calcium carbonate in the form of calcite ($CaCO_3$), the carbonized palm kernel shell have carbon in graphite form. It is therefore observed from the SEM micrographs that Figure 8 reveals little formation of pores. Figure 10 shows that the samples contains many pores than samples A and B. it could be seen that it comparatively contains more element of carbon.

4. CONCLUSION

Clay bonded carbon refractory have been produced and properties investigated. From the results obtained, the following conclusions are drawn:

- ✓ *The major phases in the raw Ifon clay sample are Kaolinite, Microcline, Muscovite/Illite, Quartz and Plagioclase Albite.*
- ✓ *The porosity of the sintered composite samples as well water adsorption reduces with increase in clay content.*
- ✓ *The cold crushing strength, young's modulus and absorbed energy of the samples increases with increase in clay content.*
- ✓ *The optimum combination of mechanical properties is achieved in a sample with composition of 40 wt% carbonized palm kernel and 60% clay.*

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