

## MULTISTAGE CAUSTIC LEACHING DE-ASHING OF NIGERIAN LAFIA-Obi COAL

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### Abstract

Fractions of the high ash Nigerian Lafia-Obi coal L±250 ground to pass the 250 µm sieve in three stages were subjected to proximate/ash composition analyses, hot aqueous leaching de-ashing with water and sodium carbonate in multiple stages and in a H<sub>2</sub>O-Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O sequence (with initial solution homogenization). The results obtained showed that ash contents percent of 24.60, 14.70 and 24.07 were obtained for fractions L-250(1), L-250(2) and L+250(2); respectively as against 32.55% in the as-received coal. The ash reductions obtained translate to overall average ash removal of about 38.66% at the 19.90% ash content of the concentrates blend at a good 1:20 ratio of reagent to coal. The study also showed that a three stage leaching in the sequence H<sub>2</sub>O-Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O (HSH) produced a higher leaching rate than Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O-H<sub>2</sub>O (SHH). The ash content of the concentrates blend at 19.90% is lower than 23.80% required for coal blends for Indian standard coking practice, but higher than the maximum of 10% upper limit for the conventional cokemaking practice. The reduction in ash content obtained at the atmospheric pressure treatment of Lafia-Obi coal was found to compare favourably with that of a high pressure elevated temperature autoclave leaching of an Illinois coal. Binary blend formulation between the prime coking western Canada coal and Lafia-Obi coal as-leached showed that inclusion of 16.63% of the latter was probable and this translates to reduction in cost per ton of about \$23.67. A successful upgrade of the leaching route derived to industrial scale will make Lafia-Obi coal available as a blend component for economical cokemaking.

**Keywords:** coal; ash, de-ashing; leaching; concentrate.

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### 1. Introduction

Coal is a combustible sedimentary organic rock which is composed mainly of carbon, hydrogen and oxygen. It is formed from vegetation which has been consolidated between other rock strata and altered by the combined effects of pressure, temperature and bacteria over million of years to form the coal seams. Nigeria is endowed with notable coal deposits at Ogboyoga, Okaba, Orukpa, Ezimo, Enugu and Lafia-Obi with total reportable and non-reportable reserves of 411, 635, 299, 349, 209 and 33 million metric tons, respectively. Lafia-Obi is the only medium coking of the six coals but contains very high inherent ash and sulphur [1, 2, 3].

In view of the scarcity of coking coal worldwide and its high cost in the international market, methods to upgrade low grade coals by reducing their ash and sulphur contents have been developed. These methods can be classed as physical, chemical and biological and their successful application has led to the production of coal concentrates with low ash, low sulphur and improved thermoplastic properties. The chemical leaching methods include molten caustic leaching and agitation caustic leaching and have been successfully employed to reduce the ash and sulphur contents of coals [4, 5].

Chriswell et al [6] reported the use of the molten caustic leaching (MCL) method for the removal over 90% of the sulphur and ash in coal. The molten caustic leaching method is an advanced chemical technique that involves the water washing of caustic leached coals to remove un-reacted caustic and impurities produced by reactions of oxides with the molten caustic. A counter current procedure designed for efficient washing with minimal water loss was used. The main problem encountered was the formation of massive precipitates of carbonates and this led to far lower than expected recoveries of coal concentrates.

The magnetic stirrer apparatus has one or more fixed electromagnets that generate a rotating magnetic field enclosed in housing [7]. The Stuart Scientific SM3 magnetic stirrer hot plate consists of a cast aluminum hot plate with a maximum temperature of 400°C. The unit has a built-in magnetic stirrer with variable speed up to 1,300 rpm. The SM3 model of Stuart magnetic stirrer hot plate has speed and hot plate control knobs [4, 8].

The aim of this study is to examine the response of Lafia-Obi coal to de-ashing leaching on a magnetic stirrer hot plate with sodium carbonate, a stable and cheap alternative to the commonly used sodium hydroxide.

## 2. Materials and methods

### 2.1 Materials

The collection and preparation of the samples were carried out as described in the following sub-sections.

### 2.2 Sample collection

The Lafia-Obi sample was obtained from a virgin site of Lafia-Obi coal-field on the bank of Kogi River, in Shankodi Jangwa district of Awe Local Government Area. The area is about 70 km East of Lafia, which is on Latitude 8°30' North and Longitude 8° 34' East. The coal site is about 81 km on the left side off Lafia-Obi highway. About 10 kg of the bulk samples of Lafia-Obi were removed from the top seams intersected at a depth of about 1 m from the ground surface in open pit mines A and B.

### 2.3 Sample preparation

The clean bulk samples of Lafia-Obi samples A and B were mixed in 1:1 proportions. The coal mixture was then air dried in the laboratory overnight. About 4 kg of the air dried clean mixture of the sample was thereafter crushed with Pascall Engineering 18862 primary crusher to obtain the experimental samples.

#### 2.3.1 Methods

The pulverized sample was subjected to the tests described below.

#### 2.3.2 Particle size analysis

The sample obtained from primary crushing was passed through a 250 µm sieve to obtain L-250(1) sample constituting 43.06% of the starting sample. The oversize was further subjected to secondary crushing and passed through the 250 µm sieve aperture to obtain the L-250(2) sample; while the oversize residue was labelled L+250(2) to form 49.32% and 7.62% of the starting sample; respectively.

### 2.4 Proximate analysis

The determination of moisture, volatile matter, ash and fixed carbon contents of the coal was carried out with modified forms of methods described in ASTM D 3177-89 and Francis and Peters [2].

### 2.5 Determination of coal ash Mean Basicity Index

The composition of the coal ash was determined with Philips PW 4026/458 X-ray fluorescence spectrometer. The coal samples were ashed according to the procedure described for ash content determination. About 10 g of the ash sample obtained from several ashings was finely ground to pass through 250 µm sieve. The ash sample was dried in an oven at 105°C for 1 hour and cooled to ambient temperature in desiccators. The sample was then mixed with 2.5 g of cellulose flakes binder and pelletized at a pressure of about 1.63 MPa. After sample preparation and storage in the desiccators, the machine was switched on and allowed to warm up for 2 hours. Using appropriate programs, the sulphur content of the sample was determined and displayed. Leco coal ash and coal standards were used for calibration for ash composition and sulphur content determination, respectively [9]. From the ash composition, the mean basicity index (MBI) ash was determined with the formulae 1 [10].

$$MBI = \frac{100x\%Ashx[\%Na_2O + \%CaO + \%MgO + \%Fe_2O_3]}{[(100 - \%VM)x(\%SiO_2 + \%Al_2O_3)]} \quad (1)$$

## 2.6 Aqueous Leaching of Coals

A 75 ml derivative 0.0094M aqueous solution of sodium carbonate was prepared in a 250 ml beaker. The pH was then taken with WPA CD 70 pH meter. The procedure was again repeated for 0.019, 0.038, 0.076, 0.15 and 0.30M solutions of the same volume. About 3 g of the L-250(1) sample mixed with sodium carbonate (in a 1:20 mass ratio of reagent to coal) to form 75 ml 0.019M aqueous solution in a 250 ml beaker was agitated continuously for about 5 minutes to produce a 40 g/litre solid-liquid ratio slurry. The procedure was again repeated for L-250(2) and L+250(2) samples.

The L-250(1) coal slurry prepared with lid on was then heated only on the Stuart SM3 magnetic stirrer hot plate at a setting such that a temperature of about 90°C was attained in 25 minutes. The heated coal slurry was removed from the hot plate and allowed to cool for 25 minutes. The cooled leached slurry was then filtered with a Dr Watt filter paper into a 250 ml conical flask. The coal was dried and weighed on the electronic balance. The procedure described was again repeated for the slurries of L-250(2) and L+250(2) samples.

The procedure described was further carried out for L-250(1) sample but with first stage water leaching, second stage leaching in 0.019M solution of sodium carbonate and third stage water leaching (that is, H<sub>2</sub>O-Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O (HSH) leaching sequence). The latter procedure was further repeated for Lafia-Obi fractions L-250(2) and L+250(2) (DS). The whole procedure was again repeated for L-250(2) and L+250(2) samples.

## 3. Results and discussion

### 3.1 Results

The results obtained on proximate analysis of the Lafia-Obi coal (as-received and leached), the coal ash composition, tables of blend formulations with Lafia-Obi coal as received and as leached are presented in Table 1, 2, 3 and 4 respectively; while Figures 1, 2, 3 and 4 show the effect of sodium carbonate molar concentrations on pH of leach solution, multi-stage leaching, coal concentrate % yield and comparison of the quality parameters of the Lafia-Obi concentrate with standard specifications; respectively.

Table 1 Proximate analysis, reduction in ash, volatile and increase in fixed carbon of Lafia-Obi coal

| Parameters (%)              | L±250        |
|-----------------------------|--------------|
| Moisture (R)                | 3.49         |
| Moisture (C)                | 3.15         |
| <b>Moisture (Reduction)</b> | <b>9.74</b>  |
| Volatile matter (R)         | 26.99        |
| Volatile matter (daf)       | 42.20        |
| Volatile matter (C)         | 27.36        |
| Volatile matter (daf)       | 35.56        |
| <b>VM (Reduction)</b>       | <b>15.73</b> |
| Ash(R)                      | 32.55        |
| Ash (C)                     | 19.90        |
| <b>Ash (Reduction)</b>      | <b>38.86</b> |
| Fixed Carbon (R)            | 36.97        |
| Fixed Carbon (C)            | 49.59        |
| <b>FC (Increase)</b>        | <b>25.44</b> |

*ad* = as determined (or as received)

*daf* = dried ash free

*nd* = not determined

Table 2 Main ash composition of Lafia-Obi

| Parameters (%)                                  | Lafia-Obi |
|---|-----------|
| Alumina(Al <sub>2</sub> O <sub>3</sub> )        | 19.82     |
| Silica (SiO <sub>2</sub> )                      | 39.60     |
| Sodium oxide (Na <sub>2</sub> O)                | 0.01      |
| Potassium oxide (K <sub>2</sub> O)              | 2.81      |
| Calcium oxide (CaO)                             | 0.58      |
| Titanium oxide (TiO <sub>2</sub> )              | 1.44      |
| Chromium oxide(Cr <sub>2</sub> O <sub>3</sub> ) | 0.07      |
| Manganese oxide (MnO)                           | 0.045     |
| Iron oxide (Fe <sub>2</sub> O <sub>3</sub> )    | 19.11     |
| Copper oxide (CuO)                              | 0.08      |
| Zinc oxide (ZnO)                                | 0.18      |
| Vanadium oxide (V <sub>2</sub> O <sub>5</sub> ) | 0.10      |
| Magnesium oxide (MgO)                           | 0.14      |
| Lime Ratio                                      | 0.0074    |
| Acidity Ratio                                   | 3.06      |
| Mean Basicity Index (MBI)                       | 82.28     |

Table 3 A binary blend between a Canadian prime coking coal and Lafia-Obi (as-received)

| Angle   | Canada [23] | Lafia (AR) [3] | Ash      | Cost (\$) [22] |
|---------|-------------|----------------|----------|----------------|
| 0       | 1           | 0              | 8        | 210            |
| 10      | 0.969839    | 0.03016143     | 8.740463 | 204.5709426    |
| 20      | 0.882993    | 0.117006873    | 10.87252 | 188.9387629    |
| 15      | 0.932996    | 0.067004272    | 9.644955 | 197.9392311    |
| 17.5    | 0.909553    | 0.090446695    | 10.22047 | 193.719595     |
| *16.25  | 0.921676    | 0.078324037    | 9.922855 | 195.9016733    |
| 16.875  | 0.915714    | 0.084286412    | 10.06923 | 194.8284459    |
| 16.5625 | 0.91872     | 0.081280306    | 9.995432 | 195.3695449    |

Table 4: A binary blend between a Canadian prime coking coal and Lafia-Obi  $\pm 250$  de-ashed coal

| Angle     | Canada   | Lafia $\pm 250$ | Ash      | C           |
|-----------|----------|-----------------|----------|-------------|
| 0         | 1        | 0               | 8        | 210         |
| 10        | 0.969839 | 0.03016143      | 8.358921 | 205.7062188 |
| 20        | 0.882993 | 0.117006873     | 9.392382 | 193.3429016 |
| 30        | 0.749941 | 0.250058798     | 10.9757  | 174.4016296 |
| 25        | 0.82135  | 0.178649537     | 10.12593 | 184.5674519 |
| 22.5      | 0.853517 | 0.146482616     | 9.743143 | 189.1467348 |
| 23.75     | 0.837755 | 0.162244525     | 9.93071  | 186.9028695 |
| 24.375    | 0.829631 | 0.170368567     | 10.02739 | 185.7463308 |
| *24.0625  | 0.833713 | 0.166286686     | 9.978812 | 186.3274273 |
| 24.21875  | 0.831677 | 0.168322692     | 10.00304 | 186.0375815 |
| 24.140625 | 0.832697 | 0.167303452     | 9.990911 | 186.1826806 |

### 3.2 Discussion of results

Fig.1 indicates that the pH of the aqueous solutions of sodium carbonate initially increased almost linearly with molar concentrations until about 0.076M, when the rate of pH increase reduced. The results thus suggest that increasing molar concentrations may not produce a correspondingly higher alkalinity and thus leaching rate may also not increase in direct proportion to sodium carbonate concentrations in the aqueous solutions.

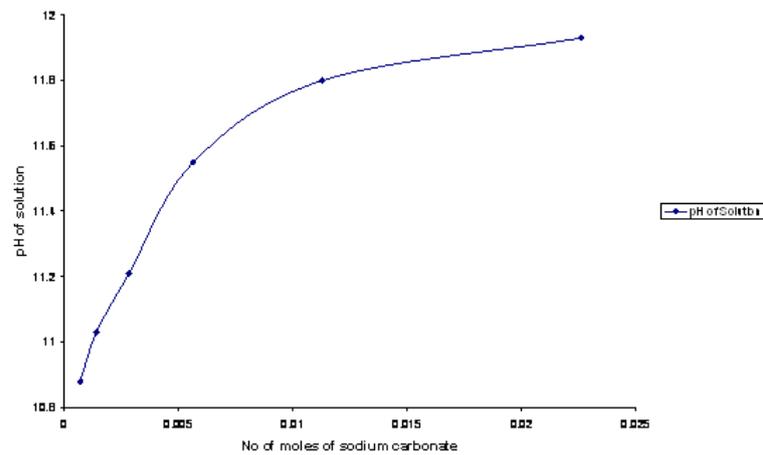


Fig. 1: Effect of molar concentrations of sodium carbonate on pH of leach solution

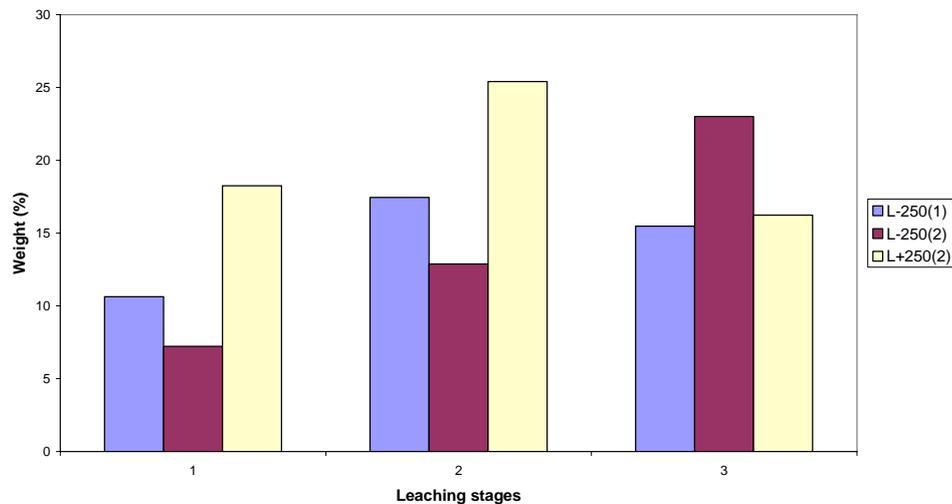


Fig. 2: Effect of three-stages ISH 1, 2 and 3 leaching of Lafia-Obi fractions (L-250(1), L-250(2) and L+250(2))

The results obtained indicate that a first stage treatment with water followed by treatment with sodium carbonate produces good gangue reduction % in Lafia-Obi coal. From the results obtained, it can be deduced that multistage leaching in the correct sequence of

H<sub>2</sub>O-Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O (H-S-H) was required for the efficient demineralization of Lafia-Obi coal fractions. The leaching of Italian Sulcis coal was conducted in two stages of potassium hydroxide and hydrogen peroxide leaching, in that order [11].

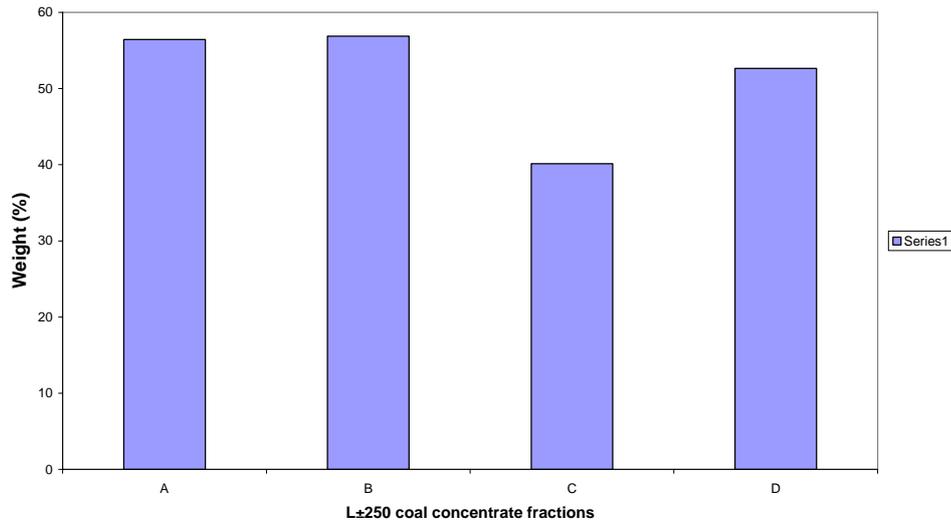


Fig. 3: Percent yields of L-250(1) (A), L-250(2) (B), L+250(2) (C) and L±250 blend

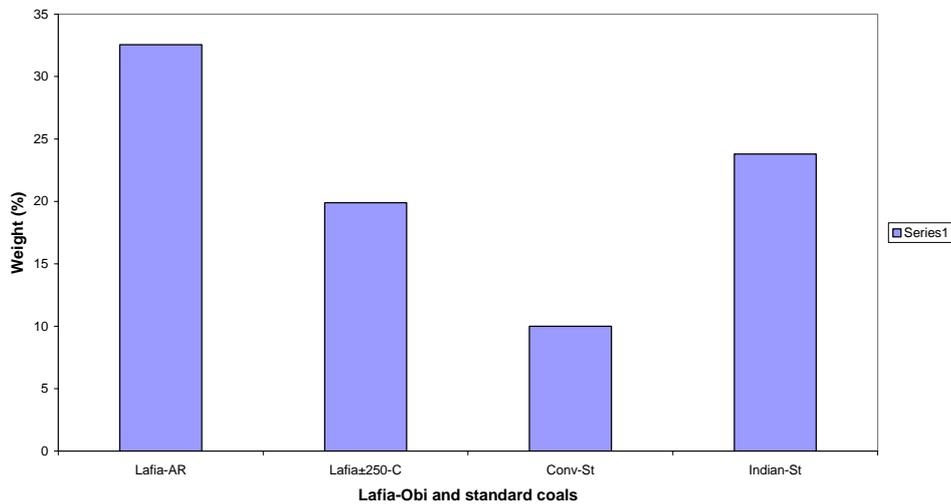


Fig. 4: Comparison of ash contents of Lafia-Obi as-received (Lafia-AR), Lafia-Obi concentrate (L±250-C), standard coal (Conv-St) and Indian standard coal (Indian-St)

From the results of the ash composition analysis, the acidity ratios calculated for Lafia-Obi blend was 3.06, while the total percentage of acidic oxides; that is, silica, alumina and titanium oxides was 60.82%. It has been reported that a high concentrations of silica and alumina causes the formation of highly viscous slag during ironmaking and the contents of both oxides are normally required to be low in both iron ore concentrates and by extension in other charge inputs such as coal/coke. For example, in direct reduction ironmaking, the contents of silica, alumina and titanium oxide in iron ore charge are required to be lower than 3.0% [12].

The Coke Strength after Reaction (CSR) was obtained from the formula:

$$CSR = 52.7 + 0.0822x(c + d) - 6.73(MBI) + 14.6R_o \quad (2)$$

where: c = % maximum contraction, d = % maximum dilatation, R<sub>o</sub> = average vitrinite reflectance.

The coke strength after reaction (CSR) value is required to be greater than 58% [13]. This formula shows that a low value of MBI is required to obtain the specified minimum for the CSR index. A decrease in the value of MBI can be obtained by reducing the overall ash content. The ash composition includes paramagnetic oxides like iron oxide and the mild slurry stirring obtained during leaching must have been due to the interaction of the stirrer rotating magnetic field with these paramagnetic particles.

Ash analysis for Lafia-Obi concentrates L±250 coal fractions leached at 1:20 Na<sub>2</sub>CO<sub>3</sub>: Lafia-Obi yielded average ash % contents reductions of 38.86. The results obtained showed that significant decrease in the ash contents of the Lafia-Obi fractions was obtained. The very high ash reduction of about 48.42% in the L-250(2) fraction that constitutes about 49.32% of the whole coal is very significant. The ash content of 14.70% in the fraction is 9.10% below the 23.80% for typical Indian coals for cokemaking and only slightly exceeds the upper limit of 10% for Ajaokuta Steel Plant specification by 4.70% [14, 15]. The reduction in the ash contents of for the Lafia-Obi fractions will appreciably raise their contents in blends for cokemaking. In addition, the finer fractions of Lafia-Obi concentrate contain average ash contents of 19.90% that is 3.90% below 23.80% ash in Indian Dugda II coal that is used in blend for metallurgical cokemaking with imported coking coals [14, 15]. An average ash increase of +29.38% was obtained at AMES Laboratory, Iowa State University for the much finer -75 μm Illinois no. 5 coal sample subjected to intense leaching in autoclave (under air/oxygen pressure at 150°C) with 0.2 M sodium carbonate in 1 hour. This result obtained shows that very high concentrations of sodium carbonate may cause an increase in ash content even under intense autoclave leaching with very fine coals [16].

A reduction in the ash contents of coals for cokemaking is critical as high ash in the blast furnace requires higher energy consumption for slagging and lowers the productivity of the blast furnace. High contents of alkali oxides causes serious incidents like frozen hearth and burnt tuyere [14, 17, 18]. The coke strength was found to reduce with increasing ash and that at an ash level of 25%, the coal tested became non-coking [15].

When sodium carbonate dissolves in water, the salt liberates sodium and carbonate ions. At the same time, the water itself hydrolyzes to produce H<sup>+</sup> and OH<sup>-</sup>. Thus, a solution containing sodium carbonate may have particles of water molecules, sodium ions, carbonate ions, hydrogen ions and hydroxyl ions. Ions of opposite charge attract each other and combine to form sodium hydroxide and carbonic acid as in Equation 3:



From the foregoing, it can be deduced that the potency of sodium carbonate in the leaching of pulverized coal may be due to the presence of sodium ions, carbonic acid and sodium hydroxide. Sodium ion may react with silica to form water soluble sodium silicate or sodium orthosilicate or sodium tetrasilicate. Sodium can also react with silica, alumina and iron oxide to produce water soluble (or partially soluble) sodium aluminosilicate, sodium aluminoferrite and calcium aluminoferrite. The sodium, sodium hydroxide, hydrogen ions and carbonic acid can also react with the oxides and sulphur in the coal.

The oxides in the coal in contact with leach solution are present as both ion (exchangeable cation that can take part in replacement reactions) and as part of discrete neutral mineral particles (that can be dissolved into solutions) [19]. The overall reactions can be assumed to consist of the following stages [20]:

- (i) Transfer of neutral oxides, sulphur in the coal particles to the interface
- (ii) Transfer of citric acid, Na<sup>+</sup> ion, NaOH, CO<sub>3</sub><sup>2-</sup> to the interface
- (iii) Reaction at the interface to produce soluble complexes, soluble complex sodium salts

Binary blend formulation between the prime coking western Canada coal and Lafia-Obi coal as-received and as-leached showed that inclusion of 7.83% and 16.63% respectively were probable; translating to reduction in cost per ton of \$14.10 and \$23.67. The results obtained indicate that blending results in a lower coking cost and that the leaching of Lafia-Obi coal may improves its inclusion in a cokeable blend with a coking coal. The further reduction in cost of \$9.57 in using Lafia-Obi concentrate is significant considering the fact that a typical coking plant uses million of tons of coal annually.

#### 4. Conclusions

The ash contents of the fractions of Lafia-Obi coal L±250 were successfully reduced by hot aqueous state leaching with sodium carbonate that is not commonly used as a leaching agent. The average ash reduction of 38.66% obtained is significant because of the low molar concentration of the reagent at 1:20 mass ratio of reagent to coal in the absence of rigorous stirring with a magnetic stirring bar. The results obtained from blend formulation indicates that the leaching of Lafia-Obi coal may improve its inclusion in a cokeable blend with a coking coal and thus reduce coking cost.

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