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MULTISTAGE CAUSTIC LEACHING DESULPHURIZATION OF A HIGH SULPHUR COAL

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Abstract

Fractions of Lafia-Obi coal (L±250) slurry in 1:20 mass ratio of reagent to coal were hot leached with sodium carbonate in three stages with H_2O-Na_2CO_3-H_2O (HSH) sequence. The analyses conducted on the leach concentrates gave sulphur(ad) % and volatile matter (daf) of 0.51 and 35.6 translating to 60.2 and 15.7 reduction percents; respectively. Ultra violet spectrophotometer analysis further confirmed the leaching of sulphur out of the coal fractions. Blend formulation calculations with the concentrates obtained in this work yielded a cokeable blend comprising 55.25% high vitrinite Canadian prime coking coal, 24.73% Okaba and 20.02% Lafia-Obi ±250 concentrates with a low sulphur content of 0.50% and a possible savings of about $70 per ton on coking coal imports. On the basis of the results obtained, the Hot Caustic Leaching (HCL) method at the normal atmospheric pressure with the associated solution homogenization pre-treatment was found to be a suitable method to cheaply upgrade the high sulphur Nigerian Lafia-Obi coal.

Keywords: coal; sulphur, leached; concentrates; blend formulation.

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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 millions of years to form the coal seams. The temperature effect mainly operates after bacteria action has ceased while pressure increases with increasing depth of burial. Coal is a fossil fuel with reserves far larger than oil and gas and that is estimated to last 119 more years. The proven reserves of coal worldwide have been estimated at about 847 billion tons, with coal being available in almost every country of the world. However, recoverable reserves are only found in about seventy countries with the biggest deposits in the United States, Russia, China and India [1, 2].

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 the only medium coking of the six contains very high inherent ash and sulphur contents of 26% to 57.8% and 2.4%, respectively. In view of its medium coking nature, there is a need to reduce the high ash and sulphur contents of Lafia-Obi coal and thus enhance its maximum participation in blends for metallurgical cokemaking [3, 4].

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 [4]. The multistage de-ashing of Lafia-Obi coal with sodium carbonate on the magnetic stirrer hot plate was reported by Adeleke *et al*, [5]. Sodium carbonate is a soda salt of carbonic acid. It occurs most commonly as a crystalline heptahydrate, which readily effloresces to form a white powder, the monohydrate. When sodium carbonate dissolves in water, the salt liberates sodium ions and carbonate ions. At the same time, the water itself ionizes slightly to form hydrogen and hydroxide ions [6]. The use of low ash/sulphur coke in the blast furnace at Ajaokuta will reduce coke consumption, improve productivity, reduce the cost of ladle metallurgy desulphurization, makes local steel production economical and lower the unit cost of steel to be produced. Furthermore, the low sulphur steel output will not be susceptible to hot shortness during forging and rolling, intergranular embrittlement during casting and temper embrittlement on heat treatment [7].

In this work, the response of Lafia-Obi coal's sulphur to multistage hot leaching with sodium carbonate was studied.

2. MATERIALS AND METHODS

2.1 Materials

The coal sample was collected and prepared as described below.

2.1.1 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 Jangwa district 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.

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

2.1.2 Sample preparation

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.

2.2 Methods

The experimental procedures used in the study are presented below:

2.2.1 Proximate analysis

The determination of moisture, ash, volatile matter and fixed carbon was carried out with modified forms of methods described by Francis *et al*, [2].

2.2.2 Determination of sulphur content

The sulphur in the whole coal and the composition of coal ash were determined with Philips PW 4026/458 X-ray fluorescence spectrometer. The coal 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 samples were determined and displayed [8].

2.2.3 Aqueous leaching of coals

The effect of sodium carbonate concentrations on the alkanity of the aqueous solutions of sodium carbonate has been reported [5]. 3 g of L-250(1) size fraction of Lafia-Obi coal was homogenized for about 5 minutes in a 75 ml aqueous solution with sodium carbonate (in a 1:20 mass ratio of reagent to coal) forming a derivative 0.019M aqueous solution of sodium carbonate. The homogenized coal slurry with the lid on was then heated only on the Stuart SM3 magnetic stirrer hot plate such that a temperature of 90°C was attained in 25 minutes. The 40 g/litre solid-liquid ratio L-250(1) coal slurry hot leached was then allowed to cool off the hot plate for the same 25 minutes. The cooled leached slurry was afterward filtered with a Dr Watt filter paper into a 250 ml conical flask. The coal concentrate was dried and weighed on the Mettler Toledo PB 153 electronic balance. The procedure described was again repeated for the slurries of L-250(2) and L+250(2) samples.

2.2.4 Multiple stages leaching

The procedure was further carried out in three stages for L-250(1) sample but with first stage water leaching, second stage leaching with sodium carbonate and third stage water leaching (that is, H_2O-Na_2CO_3-H_2O (HSH) leaching sequence). The two stage leaching was again repeated with first stage leaching with sodium carbonate, second and third stages water leaching (that is, Na_2CO_3-H_2O- H_2O (SHH) leaching sequence). The latter procedure was further repeated for Lafia-Obi fractions L-250(2) and L+250(2) samples. The weight losses obtained for the dried coal concentrates in the three-stages leaching of the coal fractions are presented in Figures 1 and 2.

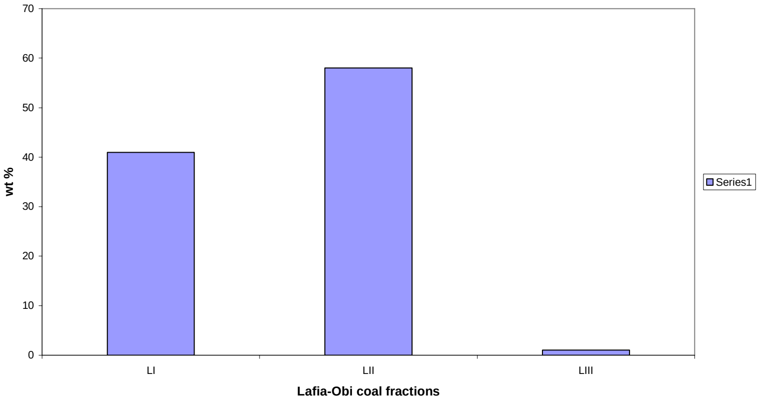

Fig. 1: Relative proportions in % of sulphur determined by UVS from Lafia-Obi coal fractions fleach iltrates

Legend: LI =L-250(1) fraction; LII = L-250(2) fraction; LII = L+250(2) fraction

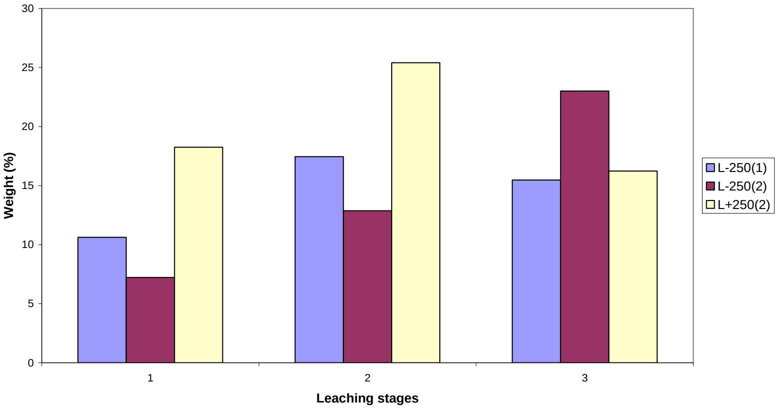

Fig. 2: Effect of three-stages ISH 1, 2 and 3 leaching of Lafia-Obi fractions (L-250(1), L-250(2) and L+250(2))

Legend:L-250(1), L-250(2) and L+250(2) = fractions of Lafia-Obi coal that comprise L±250 sample; ISH1, ISH2, ISH3 =initial solution homogenization for stages 1 and 2, respectively

2.2.5 Sulphur determination using ultra violet spectrophotometer (UVS)

The conditioning reagent was prepared by mixing 50 ml of glycerol with a solution containing 30 ml concentrated hydrochloric acid, 300 ml distilled water, 100 ml ethanol and 75 g sodium chloride. The standard solution containing 1000 ppm of sulphur was prepared by dissolving 0.1479 g of anhydrous sodium sulphate in distilled water and diluting to 1 litre. By serial dilution of the standard solution prepared, solutions at 400 ppm, 200 ppm, 100 ppm, 50 ppm, 25 ppm and 12.5 ppm were obtained.

The absorbance of each of the solution obtained by serial dilution from the standard solution was taken and a plot of the absorbance against molar concentrations gave the calibration curve. To prepare the calibration curve, 3 ml of 400 ppm solution obtained by serial dilution from the standard solution was taken into a test tube and 2 ml of the conditioning reagent was added. A spoonful of barium chloride was added to the solution mixture and it was shaken vigorously. Some of the solution was then poured into an adsorption cell and the absorbance read at 425 nm. The procedure described was then repeated for the solutions at 200, 100, 50, 25 and 12.5 ppm obtained from the standard solution. From the results obtained, the standard absorption versus concentration curve was plotted.

The absorption of the incident ultra violet radiation was determined with Heλios ɑ ultra violet spectrophotometer. 3 ml of the leaching filtrate was poured into a test tube and mixed with 2 ml of the conditioning reagent. Some quantity of barium chloride was then added to the mixture and it was vigorously shaken. Some volume of the mixture was poured into the adsorption cell and the absorption readings were taken. The % sulphur in the filtrate was then calculated using Equation 1.

$$\%\ Sulphur\ in\ \ filtrate = 0.333\,X\ \ C_F\ \ X\ \ V_F \qquad (1)$$

where: C_F = Concentrations of filtrates (ppm); V_F = Volume of filtrates (ml).

3. Results and Discussion

The results obtained in the study and the related discussion are presented below.

3.1 Results

The average results obtained for moisture, volatile and sulphur contents for Lafia-Obi±250 fractions are presented in Table 1, while Figures 1 and 2 show the quantity of sulphur leached in Lafia-Obi±250 (mg/g) and overall average percent reduction in sulphur content obtained and the weight loss effects of the three stage leaching on the Lafia-Obi fractions; respectively. The results of blend formulation calculations between Lafia-Obi concentrate, a prime coking Canadian coal and Okaba coal is presented in Table 2.

Table 1 Moisture contents, volatile and sulphur Lafia-Obi coals

Parameters (%)	L±250
Moisture (R)	3.49
Moisture (C)	3.15
Moisture (Reduction)	9.74
Volatile matter (R)	26.99
Volatile matter (daf)	42.20
Volatile matter (C)	27.36
Volatile matter (daf)	35.56
VM (Reduction)	15.73
Sulphur (R)	1.28
Sulphur (C)	0.51
Sulphur (Reduction)	60.16

Table 2 Formulated blends from Canada, Okaba (±250) and Lafia-Obi (±250) coals

Canada	OK±250 Conc	L±250 Conc	VR	ASH	Sulphur	VM	Fixed carbon	Cost/ton
0.74878	0.18810	0.063108	1.2891	8.1519	0.46529	23.147	68.6062	169.52
0.58498	0.24277	0.172238	1.1929	9.5816	0.49806	25.813	64.0904	144.83
0.56335	0.24598	0.190661	1.1834	9.8181	0.50143	26.101	63.5121	141.67
*0.5524	0.24724	0.200266	1.179	9.9411	0.50304	26.240	63.2232	140.10
0.5416	0.24826	0.210130	1.1746	10.067	0.50459	26.376	62.9347	138.52
0.49789	0.24999	0.252106	1.1593	10.601	0.51025	26.882	61.7877	132.26

LEGEND: VR = Vitrinite Reflectance (Average); VM = Volatile Matter; VR = vitrinite reflectance (average) (Source: Price et al [9], Estimated, Panaitescu [10] ; Ash = ash content (as determined); Cost = cost per ton (Source: Energy Information Administration [11]; HB Industry Report [12]; New York Times [13]) ; FC = fixed carbon.

3.2 Discussion of results

The analyses conducted on the Lafia-Obi (±250) leach concentrates gave average sulphur (ad) of 0.51% translating to reduction in sulphur content of about 60.16% at derivative 0.019M sodium carbonate. The results obtained showed that hot leaching produced a good leaching effect for sodium carbonate even at the very low concentration used. This result agrees with the observation of Chuang *et al* [14] that dilute solutions of sodium carbonate produced better desulphurization effects than concentrated ones. For -75μm Illinois no. 5 coal sample subjected to intense leaching in autoclave, the average sulphur reduction obtained was 43.13% for 0.2 M sodium carbonate. For the leaching of the Italian Sulcis coal, the 38.46% sulphur reduction obtained in the 6.50% sulphur coal is lower than the 60.16% obtained for Lafia-Obi coal [15].

The results obtained on the three stage leaching of the Lafia-Obi fractions showed that L-250(2) fraction gave the highest sulphur loss per unit of the coal leached into the filtrate. It was also observed that for L-250(2 the weight loss % increases with the leaching sequence step, while for L-250(1) and L+250(2) the step two produced the highest weight loss. The good weight losses obtained in the second step of the three stage leaching for two of the fractions indicate that caustic leaching following a preliminary water leaching may impart a higher leaching potency. The highest leaching obtained for the fraction L-250(1) in the final cleaning stage with water similarly suggests that the final water cleaning step is critical for the three steps leaching process.

The total sulphur reduction of 60.16% obtained for Lafia-Obi coal compares favourably with 16% to 63% obtained for the high temperature (100ºC to 180ºC) leaching of the Turkish asphaltite coal with sodium hydroxide at much longer duration of 4 to 16 hours [16]. However, the sulphur reduction % of 60.16 obtained in Lafia-Obi±250 by leaching is lower than 78% sulphur reduction obtained in Lafia-Obi samples by froth flotation [4, 17, 18]. Reduction in sulphur contents is critical in the production of low sulphur liquid iron for steelmaking. Low sulphur steel will not be susceptible to hot shortness [6].

The desulphurization process for the Lafia±250 micron fractions treated with 1:20 Na_2CO_3: Lafia-Obi, also caused an average volatile % content (daf) reduction of 15.73. The average volatile of 27.36% determined for the Lafia-Obi ±250 fractions fall below the upper limit of 30.30% for coals for cokemaking at Ajaokuta by -2.94% [19]. As regards the mechanisms of the leaching reaction, it has been postulated that the oxides and sulphur in the coals in contact with leached 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) [20]. The overall leaching reactions can be assumed to consist of the following stages [21]:

(i) Transfer of neutral oxides, sulphur in the coal particles to the interface
(ii) Transfer of Na^+ ion, NaOH, CO^{2-} to the interface
(iii) Reaction at the interface to produce soluble complexes, soluble complex sodium salts

The presence of sodium hydroxide in the leach solution has been found to cause pyrolysis and de-polymerization of the coal/asphaltite matter and thus sulphur removal. This might have been due to solubilization of sulphates, conversion of pyritic and some organic functional groups like thiols into soluble salts. The organic sulphur might have been removed by breaking of C-S bond. The second stage washing with water was found necessary in leaching the Sirnak asphaltite with sodium hydroxide at high temperature [22].

Using the numerical method elaborated by Adeleke *et al* [23] on the bases of data from literature, it was found that while the blending of leached Lafia-Obi coal±250 with the prime coking Canadian coal and non-coking Okaba coal gave a cost reduction of about $70 per ton while satisfying sulphur and ash requirements.

4. Conclusions

The sulphur contents of the Lafia-Obi coal fractions L±250 were successfully reduced by hot aqueous state leaching using sodium carbonate as the leaching agent in a three step process that showed the importance of the last stage of water washing of the caustic leached coal. The average sulphur reduction of 60.16% obtained at a low molar concentration of sodium carbonate at normal atmospheric pressure is significant for such a high ash coal like

Lafia-Obi coal. The blend calculation with a prime coking coal gave a cokeable blend with satisfactory sulphur content and a high possible cost reduction per ton of $70.

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