Studies on the Ash Chemistry of the Nigerian Enugu Coal as a Blend Component in Metallurgical Cokemaking.


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ABSTRACT

The Nigerian non-coking Enugu and Australian medium coking coals were subjected to proximate and ash composition analyses to determine their suitability or otherwise as blend components for metallurgical cokemaking and pulverized injection into blast furnaces. From the analysis results, ash contents of 8.10% and 8.36%, acidity ratio (AR) of 15.22 and 18.22, mean basicity index (MBI) of 1.08 and 0.90 and total alkalies percent (TA) of 0.36% and 1.24% were determined for Enugu and Australian coals, respectively. When these results are compared with those of the self-coking Bulli Australian coal, the two coals have ash contents that are acceptable to form part of blends for metallurgical cokemaking and for injection into the blast furnace. The relatively low MBI and total alkalies contents determined for the two coals also strongly indicate that coke resulting from blends containing them may have acceptable coke strength after reaction (with carbon dioxide) (CSR) values.

(Keywords: coal, ash, acidity, basicity, metallurgical, cokemaking)

INTRODUCTION

Coal can be defined as a compact stratified mass of mummified plant debris, interspersed with smaller amounts of inorganic matter and covered with sedimentary rocks. The transformation from plant tissues to coal occurs due to the effects of temperature, pressure, and the activities of bacteria. The rank of a coal is the degree of change of the chemical composition of the coal within the series of fossil fuels from peat to anthracite (Francis and Peters, 1980). The first stage in the production of coal is thus peat, progressing through brown coal to the bituminous and anthracite categories. The coking coal to produce metallurgical grade coke comes from the bituminous grade coals, which constitutes about 52% of the world’s resources of coals. However, only about 5% of the world’s supply of coals is prime coking and suitable for straight carbonization (http://www.worldcoal.org; Bujnowska and Collins, 1992).

Coal is a readily combustible sedimentary rock containing more than 50% by weight or more than 70% by volume of carbonaceous materials including inherent moisture. The largest single use of coal in the steel industry is as a fuel for the blast furnace, either for the production of metallurgical coke or for injection with the hot blast. For pulverized injection, the coal must deliver a known and consistent calorific value, be reasonably low in ash and meet environmental requirement for for sulphur and nitrogen oxide emissions. Only a certain class of coals possessing very specific properties and composition are suitable for the production of a metallurgical grade coke (http://www.steel.org).

The ash in coal is also of great importance in ironmaking. High ash in coke lowers the carbon content and also demands the use of more fluxes and hence consumes more energy for slagging. This increases coke rate and leads to lower efficiency of the metallurgical process. It has been reported that 1% increase in ash content in coke leads to an increase of 1.5 to 2% in coke rate, 1.5% in the flux rate and lowers blast furnace efficiency by 3 to 5% (Moitra et al., 1972). The simple acidity ratio is given by the formula:
\[ AR = \frac{\%Al_2O_3 + \%SiO_2}{\%Fe_2O_3 + CaO + MgO} \] (1)

while the Mean basicity index is calculated from the formula (Price et al, 1992):

\[ MBI = \frac{100 \times \% \text{Ash} \times (Na_2O + CaO + MgO + Fe_2O_3)}{[(100 - \% \text{VM}) \times (SiO_2 + Al_2O_3)]} \] (2)

Coke properties are important for the efficient operation of the blast furnace. Coke provides the carbon required for combustion and reduction process while remaining large and relatively unreactive as it passes through the blast furnace. Blast furnace performance has been found to depend on the strength of coke as measured by standard tumbler test (e.g. micum test) and coke strength after reaction (CSR) with carbon dioxide at 1,100°C (Price et al, 1992). The CSR for some Canadian coals have been successfully predicted with the formula:

\[ CSR = 52.7 + 0.0822(c + d) - 6.73(MBI) + 14.6R_o \] (3)

Where:
- \( c \) = % maximum contraction
- \( d \) = % maximum dilatation
- \( R_o \) = Average vitrinite ce

**MATERIALS AND METHODS**

Samples of Nigerian Enugu and Australian coals.

**METHODS**

The coal samples were subjected to proximate and ash analyses (Francis and Peters, 1980).

**PROXIMATE ANALYSIS**

Proximate analysis of coal and coke involves the determination of moisture content, volatile matter content, ash content and fixed carbon of coal and coke.

**Determination of Moisture Content:** The crucible was preheated at a temperature of 110°C for 1 hour. 1g of coal ground to pass 250 microns was then heated in the crucible at 110°C for 1 hour. The loss in weight accounts for the moisture content.

**Determination of Volatile Matter (VM):** The silica crucible was pre-heated in the muffle furnace for 7 minutes at 900°C and cooled. 1g of sample ground to pass 250 microns was then placed in the crucible and heated in the muffle furnace for 7 minutes at 900°C. The loss in weight accounts for the volatile matter of the coal sample.

**Ash Content Determination:** The silica crucible was pre-heated in a muffle furnace at 825°C for 1 hour. It was then cooled and weighed. 1g of sample ground to pass 250 microns was placed in the crucible and heated in the furnace at 825°C for 1 hour with the lid on. It was then cooled in the desiccators and weighed. The incombustible residue constitutes the ash content.

**Fixed Carbon Determination:** Fixed carbon of coal or coke was determined by calculation with the relation:

\[ \% \text{Fixed carbon} = 100 - \% \text{moisture} - \% \text{Ash} - \% \text{VM} \] (4)

**ASH ANALYSIS**

The ash of the sample was obtained by igniting the sample at the temperature of 825°C for 1 hour until the sample was completely ashed. The ash obtained was then analyzed for a number of parameters. Both classical and instrumental methods of analysis were used. Classical method was used to analyze Al₂O₃, SiO₂, CaO, MgO, and Fe₂O₃ while instrumental method (i.e., an Atomic Emission Spectrophotometer (AES)) was used for Na and K.
**Determination of Silica in Ash:** 0.2g of the ash sample was weighed into a platinum crucible and mixed thoroughly with the fusion mixture and then covered up with some of the fusion mixture. It was fused at a temperature of 950 °C in a muffle furnace and allowed to cool. The fused mass was extracted into a 400ml beaker using 50ml of 1:1 HCl.

The extract was dehydrated on the hot plate using asbestos pad, after which it was cooled and 10ml concentrated HCl was added. Distilled water was used to make up the volume to the 50ml mark in the beaker. It was allowed to boil and filtered through No 541 filter paper. The residue was washed with 1:4 HCl 3 times and with hot water several times until the residue was free from HCl. The filter paper was folded into the platinum crucible and ignited at a temperature of 950 °C to constant weight in 20 minutes.

The crucible was then cooled in the desiccators and weighed as W1. Eight drops of 1:1 H2SO4 and 15ml HF were added to the residue in the crucible and it was heated in a sand bath placed on a hot plate to ensure slow evaporation. At the end, a copious fume was observed leaving the dried mass. The residue was now ignited in a muffle furnace at 950 °C for 20 minutes. It was cooled in a desiccators and the crucible weighed as W2. The percent weight of silica was calculated with the formula:

$$\text{% SiO}_2 = \frac{(W1 - W2) x 100}{W_s}$$  \hspace{1cm} (5)

Where: $W1 =$ Weight of the platinum crucible with the material before hydroflourisation

$W_s =$Weight of the sample

**Determination of Alumina in Ash:**
0.1g of the ash sample was weighed into a nickel crucible and 10 pellets of sodium hydroxide and a pinch of sodium carbonate was added. The mixture was melted over hot plate and finally fused over a low flame at 700 °C for 15 minutes.

The crucible was set aside and allowed to cool in air. When cooled, the crucible along with the content was dropped in a 250ml beaker and 100ml of hot distilled water was slowly added and boiled for 10 minutes. The crucible was removed with a glass rod and washed thoroughly with water into the beaker. The hot solution was filtered with No 40 filter paper into a 500ml conical flask.

The precipitate was then washed with hot water for 6 times to ensure that no sodium aluminate remains trapped in the precipitate. The filtrate was acidified with hydrochloric acid and 25ml standard EDTA was also added. The pH was adjusted to 5.5 with ammonium hydroxide and hydrochloric acid and the solution boiled for 15 minutes.

The solution was allowed to cool and 25ml acetic acid ammonium acetate buffer solution was added. The pH was checked and adjusted to 5.5 and drops of xylene orange indicator was added and a lemon color developed. Standard zinc acetate was used to titrate the solution. The color changed from lemon yellow to purple indicating the end point. From the titre value the $Al_2O_3$ percentage was calculated with the formula:

$$\text{% Al}_2O_3 = \frac{(A - T) x X x 100}{W_s}$$  \hspace{1cm} (6)

Where:

$A =$ ml of zinc acetate equivalent to 25ml EDTA solution.

$B=$ ml of zinc acetate solution required for titration after adding 25 ml EDTA solution to the 5 ml standard $Al_2O_3$ solution

$T =$ The titre value of zinc acetate with the sample under experiment.

**Determination of Calcium and Magnesium Oxide:**
0.2g of the sample was weighed into a 25ml beaker. 20ml of 1:1 HCl was added and digested on the hot plate. The solution was then filtered into a 250ml volumetric flask using filter paper No 541. The filter paper was washed several times with hot water, and the solution was cooled and made up to mark.

For calcium: 25ml of the aliquot was pipetted into a 250ml conical flask and 100ml of distilled water added. 30mg of MgCl2 + 4ml 8M KOH was added to the solution to precipitate the magnesium hydroxide. After two minutes, 30mg of potassium cyanide and hydroxylamine
hydrochloride were added and allowed to dissolve by constant stirring. The 0.01M EDTA was titrated against the solution using calcon indicator until the color changes from pink to blue. The percent CaO was calculated with the formula:

$$\%\text{CaO} = \frac{V_{EDTA} \times 0.5608}{W_s}$$  (7)

Where:

- $W_s$ = Weight of sample
- $V_{EDTA}$ = Volume of EDTA

For Magnesium: 25ml of the aliquot was pipetted into a 250ml conical flask. 100ml distilled water and 5ml buffer solution was added. 30mg each of potassium cyanide and hydroxylamine hydrochloride were added and allowed to dissolve by constant stirring. 0.01M EDTA was titrated against the solution using Erichrome Black T indicator until the colour changes from wine red to blue. The percent MgO was calculated with the formula:

$$\%\text{MgO} = \frac{V_{EDTA} \times 0.4032}{W_s}$$  (8)

**Determination of Iron Oxide:** 0.2g of the sample was weighed into a dry 250ml conical flask and about 3 drops of distilled water was added to moisten it. 25mls of concentrated HCl was added and swirled for proper mixture. 2 drops of HF was added and the flask placed on a hot plate. 5% SnCl$_2$ was added until the solution turned colorless.

The flask was covered with a silica crucible lid and boiled on a hot plate until dissolution was completed. The flask was removed from the hot plate and the crucible lid and the inside wall of the conical flask was rinsed into the solution. 5% K$_2$MnO$_4$ solution was added until the yellow color of ferric ion appeared. The solution was heated to boiling and 15% stannous chloride solution was added to reduce the ferric ion. This was evident of (1:3) H$_2$SO$_4$ was added and the solution was mixed by shaking and distilled water was added until the total volume was approximately 100mls. The flask was cooled properly in a water bath. Then, 10mls of 2% mercuric chloride solution was added, mixed and the solution mixture was allowed to stand for 5 minutes. 10ml of 0.02% Fe indicator in H$_3$PO$_4$ (1:4) was added. The solution was then titrated against 0.1N K$_2$Cr$_2$O$_7$. The percent Fe was calculated with the formula:

$$\%\text{Fe} = \frac{V_1 \times V_2 \times 100}{W_s}$$  (9)

Where:

- $V_1$ = Titre of K$_2$Cr$_2$O$_7$
- $V_2$ = Volume of K$_2$Cr$_2$O$_7$

**Determination of Sodium and Potassium Oxide:** 0.5g of the sample was weighed into a Teflon beaker; 10mls each of concentrated HCl, HNO$_3$, and 5ml of HOCl$_3$ was added. The mixture was heated on a hot plate in a flame cupboard to incipient dryness. It was allowed to cool and 10ml of distilled water was added and boiled on the hot plate. The solution was filtered using a No. 540 filter paper into 100ml volumetric flask. The residue was washed several times with distilled water to ensure thorough washing of the residue. The residue was discarded and the volume of the solution (filtrate) was made up to mark. The emission of the solution was read using the 405 flame photometer machine.

The concentration of Na and K in the sample was determined from the Emission versus concentration graph prepared from Na and K standard at concentrations: 0, 2.5, 5.0, 7.5 and 10 $\mu$g/ml. The percent sodium and potassium was then calculated with the appropriate formulae. The results of the analyses are presented in Table 1 and discussed below.

**Table 1: Ash Chemistry of Nigerian Enugu and Australian Coals.**

<table>
<thead>
<tr>
<th>S/N</th>
<th>Coals</th>
<th>A</th>
<th>VM</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>AR</th>
<th>MBI</th>
<th>TA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ENG</td>
<td>8.1</td>
<td>46.93</td>
<td>0.14</td>
<td>0.22</td>
<td>1.40</td>
<td>0.20</td>
<td>2.89</td>
<td>61.20</td>
<td>7.13</td>
<td>15.22</td>
<td>1.08</td>
<td>0.36</td>
</tr>
<tr>
<td>2</td>
<td>AC</td>
<td>8.36</td>
<td>36.71</td>
<td>0.27</td>
<td>0.97</td>
<td>0.72</td>
<td>0.30</td>
<td>4.05</td>
<td>52.60</td>
<td>39.80</td>
<td>18.22</td>
<td>0.90</td>
<td>1.24</td>
</tr>
<tr>
<td>3</td>
<td>BSC</td>
<td>9.6</td>
<td>26.6</td>
<td>0.38</td>
<td>1.20</td>
<td>1.80</td>
<td>0.41</td>
<td>4.3</td>
<td>52</td>
<td>36</td>
<td>13.52</td>
<td>1.20</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Note: A=Ash content, VM(daf)=Volatile matter (dried ash free), AC=Australian coal, ENG=Enugu coal, TA=Total % alkali oxides, BSC=Bulli standard coal (Source: BHP Integrated Steel Publication (1998))
DISCUSSION OF RESULTS

The ash contents of 8.10% and 8.36% determined for Enugu and Australian coals fall within the range of 7.20% and 9.60% for main coals carbonized in Japan to produce coke (Katsuhiko et al, 1987). The ash content of 11.79% for the Chinese Aieweihe Gou coal exceeds those of Enugu and Australian coals, but the 3.49% ash content of the Chinese Wugong coal is far lower (Zhou, 1987). The ash contents of 3.94% to 8.11% for coal blends carbonized at the Chinese Wuhan Iron and Steel University is similar to the ash contents of both Enugu and Australian coals (Lu and Li, 1987). It has been observed that ash in coke has a critical effect on iron quality, slag composition and the desulphurization process.

The control of coke ash is done by a careful selection of coals of low ash contents (Pluzhnikov and Tsymbal, 1983). The ash contents for both Enugu and Australian coals are also below the upper limit of 12% for coals for metallurgical cokemaking at the Nigerian Ajaokuta Steel Plant (Raw Materials Specification, 1994). The ash content of 9.6% determined for the self-coking Bulli standard coal exceeds the ash contents for the two coals analyzed. These results strongly indicate that the two coals can take part in blends for metallurgical cokemaking and as coals for pulverized injection into the blast furnace with no adverse effects occasioned by ash content on the blast furnace operational efficiency.

The K₂O content of 0.22% and 0.97% for both Enugu and Australian coals exceed the upper limit of 0.18% required for coke production at the France Usinor’s steel plant (Garin et al, 1987). The total alkali percent of 0.36% and 1.24% for Enugu and Australian coals are lower than the upper limits of 3.94% to 7.04% for coals injected into the blast furnace in the United Kingdom to reduce the effects of coke degradation due to the re-circulating alkalis (Willmers and Bennington, 1992). The total alkali content of 1.58% for the standard Bulli coal exceeds those of the two coals. The alkalis, also called tramp elements disturb the regularity of the furnace operation and causes inconsistency of iron quality. Sometimes, they induce major furnace incidents such as frozen hearth and burnt tuyere (Poos, 1992).

The relatively low contents of the alkalis suggest that the two coals can safely form part of blends for cokemaking and are injectable into the blast furnace (to reduce coke rate) without adverse effects on the CSR value of the resulting coke.

The simple lime ratio \( \frac{CaO}{SiO_2} \) of 0.023 and 0.014 for Enugu and Australian coals, respectively; are far lower than about 1 and 2.5 to 4.0 required for blast furnace and Basic Oxygen furnace operations, respectively (http://www.eere.energy.gov/industry/steel).

The lime ratio value of 0.035 for the standard Bulli coal is also similar to those of the two coals. These results show that the required lime ratio of 1 will be obtained by the addition of lime to the charge during the blast furnace ironmaking process.

The MBI values of 1.08 and 0.90 determined for Enugu and Australian coals are lower than 1.20 determined for Bulli prime coking coal with a measured CSR of 72% which deviate by only 5 units from the 67% obtained by using Equation 3. Equation 3 shows that the CSR value will decrease with decreasing value of MBI. These results strongly indicate that the ash chemistry of both Enugu and the Australian coals may not adversely affect the CSR of coke produced from blends containing the two coals, particularly when the prime coking base coal has good dilatation and average vitrinite reflectance values.

CONCLUSIONS

The ash chemistry of the Nigerian Enugu and Australian coals showed that the two coals have ash contents that are acceptable for to form part of blends for metallurgical cokemaking and for injection into the blast furnace. The relatively low MBI and total alkalis contents determined for the two coals also strongly indicate that coke resulting from blends containing them may have acceptable coke strength after reaction (with carbon dioxide) (CSR) values.

REFERENCES


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