

Physico-Chemical Characterization and Speciation of Sulphur of Nigerian Coal Samples

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ABSTRACT

Studies of physico-chemical characterization, and chemical speciation of sulphur of seven Nigerian coal samples have been undertaken. The seven coal samples originated from South-east, North-central and North-east of Nigeria where there are proven economic deposits of this mineral. Moisture content, bulk density, percentage ash and loss of mass on ignition of all the coal samples were determined. The ultimate analysis of the raw coal, the corresponding coal ash as well as sulphur content of all samples were carried out with the aid of X-ray fluorescence technique (XRF). The major elements were Fe, Ca and S while the minor metals were K, Sc, Zn, Ni, Ti and Zr. Other metals including Ga, Cu, Mn, Cr and V were found in traces. The Nickel/Vanadium ratio which is a means of providing information on the source rock depositional environment ranged between 8.8 - 32.9. Three different source rock depositional environments were deduced for the coals from their nickel/vanadium ratios, while the calculated values of $V/(V+Ni)$ suggested that they were all formed under oxic condition. The three chemical species of sulphur, sulphate, pyritic and organic sulphur in the seven coal samples were determined using the ASTM method.

Keywords: Sulphur Speciation; Nigerian Coal; X-Ray Fluorescence Analysis; Heavy Metals

1. Introduction

Coal can be defined as a chemically and physically heterogeneous, “combustible”, sedimentary rock consisting of both organic and inorganic materials. Organically, coal consists primarily of carbon, hydrogen, and oxygen, with lesser amounts of sulphur and nitrogen. Inorganically, coal consists of a diverse range of ash-forming compounds distributed throughout the coal [1].

Coal is classified into four general categories, or “ranks”. They range from lignite through subbituminous and bituminous to anthracite, reflecting the progressive response of individual deposits of coal to increasing heat and pressure. The carbon content of coal supplies most of its heating value, but other factors also influence the amount of energy it contains per unit of weight [2].

The sulphur content of coal varies considerably with the nature and origin of the fossil deposits [3]. Sulphur in coal is present in both inorganic and organic forms. The inorganic sulphur in coal consists predominantly of sulphides (pyrite (FeS_2), sphalerite (ZnS), galena (PbS), arsenopyrite ($FeAsS$) and others) and sulphates (barite ($BaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), and a number of iron sulphates and others) [4]. Pyrite is generally the preponderant inorganic sulphur in coal.

Particles of pyrite are randomly distributed as crystals throughout the coal but are not bound to it [5].

The organic sulphur in coal is covalently bound into its large complex structure and is difficult to remove physically or chemically, in contrast to pyritic or inorganic sulphur [6]. The organic sulphur in coal exists as both aliphatic and aromatic or heterocyclic forms, which can be classified into four groups [7]: aliphatic or aromatic thiols (mercaptans, thiophenols); aliphatic, aromatic, or mixed sulphides (thioethers); aliphatic, aromatic, or mixed disulphides (dithioethers) and heterocyclic compounds or the thiophene type (dibenzothiophenes).

The utilization of coals for both energy production and various coal conversion processes is limited by the presence of sulphur in the coal. The high sulphur dioxide emissions caused by the utilization of coals as a major fossil fuel leads to worldwide environmental problems [8]. When coal is burnt its sulphur content combines with oxygen to form sulphur dioxide (SO_2), which contributes to both pollution and acid rain [9]. Acid rain resulting from SO_2 has a harmful effect on agriculture and destroys the ecological balance [10]. The presence of sulphur in coal also reduces the quality of metallurgical coal [11,12]. Therefore, it is necessary to remove the mineral matter and sulphur from coal prior to its utilization.

Nigeria has major coal resources that have not been

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well explored or exploited. The coal reserves in Nigeria are estimated to be in excess of 2.5 billion tonnes and they are mainly of sub-bituminous type. The government has prioritized the use of these resources in order to deal with the country's power supply problems [13].

Several studies have been carried out on the trace metal characterization of coals from various locations in Nigeria using mainly Atomic Absorption spectrometry (AAS). There has been important underestimation of the levels of metals due to incomplete wet digestion of the coal materials on one hand and as a result of limited capacity of this technique when compared to modern instrumental techniques such as XRF. Moreover, most of the works reported concerned the raw coal samples and with lack of information on the coals' ashes residues. This study has therefore been conceived with the view of carrying out comprehensive trace metal analysis of not only the coal materials but in addition, their corresponding ashes residues.

Furthermore, there is dearth of information on the chemical forms of sulphur in Nigerian coals which is a pre-condition for assessing its suitability for use in a coal-fired plant. The objectives of the present investigation were therefore to carry out physico-chemical characterization of some Nigerian coal samples, determine the various chemical forms of sulphur in these coals.

2. Experimental Section

2.1. Sample Collection

All coal samples used were obtained either from the Nigerian Coal Corporation, Enugu or the National Metallurgical Research Centre, Jos, Nigeria. The coal samples originated from the following seven coal mining fields in Nigeria:

Onyeama(OYM), Okpara (OKP), Okaba (OKB), Iva (IVA), Chikila (CKL), Lafia Obi (LFB) and Jankwa Shankodi (JKS).

2.1.1. Sample Pre-Treatment

The selected lumps of coal samples were air-dried and then pulverized with clean mortar and pestle and sieved

into selected mesh powder. The powdered samples with particles diameter less than 50 μ m were retained for all investigations.

2.1.2. Physico-chemical characterization of Materials

The physico-chemical parameters analysed for in the coal samples were moisture content, bulk density, loss of mass on ignition, ash content, sulphur and metals.

Moisture content was determined by heating to a constant weight using a MINO/53/CLAD oven at a temperature of 105°C for three hours [14]; The bulk density of coal samples was determined following a simple displacement procedure based on the Archimede's principle [14]; The loss of mass on ignition and the ash content were determined by heating the sample to constant weight at 650°C for three hours in the carbolite ELF 11/148 muffled furnace [14]. The elemental composition of the coal samples were carried out with the aid of Energy Dispersive-X-ray fluorescence spectrophotometer (ED-XRF), Philip's model 12045 B4/3. The total sulphur in coal samples was determined with ED-XRF. While Sulphate-S and Pyritic-S in the coals were carried out using standard ASTM methods [15]. Organic sulphur was determined by difference.

3. Results and Discussion

Physico-chemical characteristics of seven different coal samples from Nigeria are summarized in **Table 1**.

Chikila coal has the highest moisture content with value of 7.1% while Jankwa Shankodi has the lowest moisture content of 1.3%. Onyeama, Okpara and Iva coals have moisture contents of 2.6%, 3.1% and 4.1% respectively which are very close to the value of 3.5% earlier reported by Onwu [16] for Enugu coals.

3.1. Total Elemental Analysis

The results of elemental analysis of the coal obtained with the aid of ED-XRF are given in **Table 2**.

It is evident from the ED-XRF results that there is variation in abundance of various elements in all the coal samples investigated. In Onyeama coal, sulphur occurred

Table 1. Proximate analysis of Nigerian coal samples.

Samples	Moisture content (%)	Bulk density (g/cm ³)	Loss of mass on ignition (%)	Ash content (%)
Onyeama	2.6	0.71	83.7	16.3
Okpara	3.1	0.69	93.4	6.7
Okaba	4.3	0.73	91.0	9.4
Iva	4.1	0.69	93.4	6.7
Chikila	7.1	1.37	75.7	23.4
Lafia obi	1.5	1.29	87.4	12.9
Jankwa shankodi	1.3	1.20	79.9	20.1

Table 2. Sulphur and metals analysis of some Nigerian coal samples.

Element	Onyeama	Okpara	Okaba	Iva	Chikila	Lafia obi	Jankwa S.
S (ppm)	3015 ± 249	8614 ± 1414	7002 ± 1204	2996 ± 255	7811 ± 398	3503 ± 281	4511 ± 286
K (ppm)	213 ± 12.1	667 ± 73.4	792 ± 76	106 ± 12	401 ± 19	185 ± 16	291 ± 20
Ca(ppm)	533 ± 41	9751 ± 100	8201 ± 101.8	3852 ± 10.2	1.604 ± 0.01	355 ± 41	5966 ± 121
Sc(ppm)	32.8 ± 4.6	1223 ± 176	1061 ± 159	168.9 ± 19.1	414 ± 40.3	64.2 ± 11	84 ± 9
Ti (ppm)	784 ± 17.1	15,010 ± 0.03	13,000 ± 0.02	1559 ± 26	1342.1 ± 34	356.1 ± 15	691.7 ± 21
V(ppm)	8.11 ± 1.7	137 ± 7.81	106.3 ± 7	15 ± 3	15.2 ± 1	9 ± 3	9.1 ± 1
Cr(ppm)	11 ± 1.4	86 ± 8.03	50.6 ± 6.1	13.1 ± 1.1	21.1 ± 4	14.9 ± 2	13.01 ± 3
Mn(ppm)	45.81 ± 2.4	130.2 ± 8	86 ± 5.8	155.8 ± 5	69 ± 3	62.3 ± 2	51.97 ± 3
Fe (%)	7.11 ± 0.051	5.02 ± 0.051	5.585 ± 0.07	7.771 ± 0.04	7.1 ± 0.03	9.07 ± 0.04	8.72 ± 0.031
Ni(ppm)	87.1 ± 10	1450.8 ± 69	933.1 ± 53.02	149.2 ± 14.1	277 ± 21	296 ± 21	158 ± 17
Cu(ppm)	63 ± 5.2	290.3 ± 21	279.7 ± 18.4	74.8 ± 6.3	88.1 ± 5.9	64.9 ± 6.2	81 ± 9
Zn(ppm)	231 ± 17.2	861 ± 55	1081 ± 57	199 ± 18	529.93 ± 29	463 ± 27	465 ± 27
Ga(ppm)	77 ± 5.6	345.3 ± 25.2	290.8 ± 22	84.01 ± 8.8	69.2 ± 7	69 ± 6.4	50.6 ± 4.4
Zr(ppm)	178 ± 8	219 ± 21	144.6 ± 17.8	99.02 ± 9	42.01 ± 5.1	24.1 ± 4	33.1 ± 5

as the major element, while K, Ca, Ti, Zn and Zr occurred as minor elements and Sc, V, Cr, Mn, Fe, Ni, Cu and Ga occurred in trace elements. S, Ca, Sc and Ni are present as major elements while K, V, Mn, Cu, Zn, Ga, Zr occurred as minor elements and Ti, Ga and Fe occurred as trace elements in Okpara coal. Okaba coal from Kogi state has S, Ca, Sc, and Zn as major elements while K, V, Ni, Cu, Ga and Zr occurred as minor elements and Ti, Cr, Mn and Fe are the trace elements present. In Iva coal, S, Ca, and Ti occurred as major elements while K, Sc, Mn, Ni and Zn occurred as minor and V, Cr, Fe, Cu, Ga and Zr occurred as trace elements.

Chikila has S and Ti as major elements while K, Sc, Ni and Zn are the minor elements and Ca, V, Cr, Mn, Fe, Cu, Ga and Zr are the trace elements present.

Sulphur is the only major element while K, Ca, Ti, Ni and Zn are present as minor element and Sc, V, Cr, Mn, Fe, Cu and Ga are present as a trace element in the Lafia obi coal. In Jankwa shankodi S and Ca are major elements present while K, Ti, Ni, and Zn are present as the minor elements and Sc, V, Cr, Mn, Fe, Cu, Ga and Zr are the trace element present. It is important to note that significantly higher values were measured for all metals when compared to some previous studies [17-19]. This could be adduced to the inefficiency of the digestion procedures adopted by these authors prior to AAS analysis. This was unlike the XRF technique used in this study which enabled a direct analysis of solid materials and thus, avoiding a preliminary acid digestion of coal samples. It is also worthy of note that some coal samples (Iva, Okpara, Chikila, Okaba and Onyeama) are very rich in titanium metal and this could be an indication of presence of titanium-rich minerals such as TiO_2 and $FeTiO_3$ [19,20]. Okaba and Okpara also exhibited high concen-

tration of zinc and nickel. The high concentration of zinc could be an indication of the presence of sphalerite mineral in these areas [21] In terms of the degree of the elemental analysis using, it is observed that Jankwa Shankodi has the highest total metal concentration (102600.0 ppm) while Onyeama has the least (12,382 ppm). In terms of degree of mineralization, the results show that the three coal samples (Chikila, Lafia obi and Jankwa shankodi) from the northern region of the country are highly mineralized based on their total metal content.

The presence of Vanadium in traces (9.0 - 106.3 ppm) for all the coal samples is an indication of low maturity and marine/terrestrial sourced coal [19].

The values of Ni/V ratio are presented in **Table 3** and they range between 8.8 - 32.9. Ni/V ratio has been used by several authors as a means of providing information on the source rock depositional environment [18,19].

The seven coal types investigated in this work appear to fall into three distinct groups based on Ni/V ratio. Onyeama, Okpara, Okaba and Iva coals with lowest and practically the same Ni/V ratio can be put in the same group. These coal samples can therefore be considered to

Table 3. The ratios of Ni/V and V/(V+Ni).

Samples	Ni/ V	V/V+Ni
Onyeama	10.7	0.09
Okpara	10.6	0.09
Okaba	8.8	0.1
Iva	9.9	0.1
Chikila	18.2	0.05
Lafia obi	32.9	0.04
Jankwa shankodi	17.4	0.05

have the same depositional environment.

The second group consists of Chikila and Jankwa shankodi with Ni/V ratio of almost twice the Ni/V ratio of the first group would also be considered to the same depositional environment. And lastly, Lafia obi coal with Ni/V ratio of 32.9 which is thrice the value of the first group can be said to have a distinct depositional environment.

It is important to mention that the Ni/V ratio calculated for Onyeama, Okpara and Okaba were much greater than the value earlier reported [19].

Furthermore V/V + Ni ratios are generally low for all the coal samples and this suggest that they were all formed under toxic conditions [19].

3.2. Sulphur and Metal Analysis of Ashes from Coal Samples

The results of elemental analysis of the ashes of the coal samples are presented in **Table 4**.

The coal ash elemental analysis gives the following concentrations.

Vanadium concentration ranges from 8 to 137 ppm with an average of 42.71 ppm. Chromium concentration ranges from 12 to 86 ppm with an average value of 29 ppm. The concentration of manganese ranges between 16 and 154 ppm with an average value of 78.14 ppm and the

highest concentration was found in Iva coal while the lowest concentration was recorded in Lafia obi coal. Concentration of Nickel ranges from 86 to 1451 ppm with the average value of 475.57 ppm; highest concentration of Nickel was recorded in Okpara coal and the least in Oyeama coal. The concentration of Zinc ranges between 197 to 1078 ppm with the average of 541 ppm. Iron concentration ranges from 4.92% to 8.26% with an average value of 6.93%. It was revealed from this work that coal beds are very rich source of some metals such as Ni, Ti, Cu, Fe and Cu. This indicates that the ash residue after burning would be a very good source of these metals and they can also be used to manufacture some other chemicals [19].

The sulphur content of the ashes is generally lower than values measured in the raw coal samples. The values in the ashes range from 2441 - 8247 ppm. The variation follows same trend as observed for the raw coal samples. The highest value was recorded for Okpara coal while the lowest was recorded for Lafia obi coal. The high level of Sulphur in the ash is an indication of the predominance of inorganic Sulphur (Sulphate and Pyritic Sulphur) in all the coal samples.

The analytical results obtained for the three chemical forms of sulphur in the coal samples are summarized in **Table 5**.

Table 4. Total metal analysis of coal ash.

Elements	Onyeama	Okpara	Okaba	Iva	Chikila	Lafia obi	Jankwa shankodi
S (ppm)	2577 ± 222	8247 ± 1372	6476 ± 1157	2841 ± 236	6219 ± 387	2441 ± 256	3325 ± 255
K (ppm)	200 ± 11	660 ± 73	791 ± 76	102 ± 8	329 ± 19	178 ± 13	285 ± 14
Ca(ppm)	532 ± 40	9749 ± 100	8195 ± 100	3847 ± 100	15,200 ± 0.01	338 ± 37	5643 ± 100
Sc(ppm)	33 ± 5	1221 ± 175	1059 ± 158	168 ± 19	413 ± 40	63 ± 11	83 ± 10
Ti (ppm)	784 ± 17	14,200 ± 0.03	12,400 ± 0.02	1557 ± 26	1341 ± 32	356 ± 13	691 ± 18
V (ppm)	8 ± 1	137 ± 8	106 ± 7	15 ± 1	15 ± 1	9 ± 1	9 ± 1
Cr (ppm)	10 ± 1	86 ± 8	50 ± 6	13 ± 1	18 ± 2	14 ± 1	12 ± 1
Mn (ppm)	45 ± 2	128 ± 8	85 ± 6	154 ± 3	67 ± 3	16 ± 2	52 ± 2
Fe(%)	8.21 ± 0.03	4.92 ± 0.05	5.50 ± 0.05	7.76 ± 0.03	6.22 ± 0.03	8.26 ± 0.04	7.61 ± 0.03
Ni(ppm)	86 ± 8	1451 ± 69	932 ± 53	150 ± 14	275 ± 18	294 ± 18	141 ± 11
Cu(ppm)	51 ± 5	289 ± 19	278 ± 18	74 ± 6	85 ± 6	65 ± 6	72 ± 6
Zn(ppm)	206 ± 16	854 ± 53	1078 ± 57	197 ± 16	528 ± 26	461 ± 25	463 ± 25
Ga(ppm)	75 ± 5	345 ± 25	290 ± 22	83 ± 8	69 ± 7	69 ± 6	50 ± 5
Zr(ppm)	177 ± 8	219 ± 21	144 ± 17	99 ± 9	42 ± 5	24 ± 4	33 ± 4

Table 5. Concentration (%) of various chemical forms of sulphur in Nigerian coal samples.

Samples	Total sulphur	Sulphate-S	Pyritic-S	Organic-S
Onyeama	0.302	0.082	0.176	0.054
Okpara	0.861	0.469	0.356	0.036
Okaba	0.700	0.337	0.311	0.052
Iva	0.300	0.008	0.276	0.016
Chikila	0.781	0.012	0.610	0.159
Lafia obi	0.350	0.002	0.242	0.106
Jankwa S.	0.451	0.047	0.286	0.118

The results of sulphur speciation revealed that pyritic-sulphur is by far the most important form in Onyeama (58.2%), Iva (92%), Chikila (78.1%), Lafia obi (69.1%) and Jankwa shankodi (63.4%) coals. Sulphate-sulphur constitutes 54.5% and 48.1% of total sulphur in Okpara and Okaba coals respectively. Organic-sulphur is generally very low in the coal samples except in Chikila, Lafia Obi and Jankwa Shankodi where it constitutes 20.4%, 30.3% and 26.2% of the total sulphur respectively.

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