



COMPARATIVE CHEMICAL AND TRACE ELEMENT COMPOSITION OF COAL SAMPLES FROM NIGERIA AND SOUTH AFRICA

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ABSTRACT

Background-The increasing use of coal as an energy source, the management of the resulting fly ash and the environmental issues and impacts of the trace elements released from coal combustion have become a great concern to life preservation and sustainability. **Objectives**-The objective is to chemically, geochemically and mineralogically characterise coals from two contrasting environments (Nigeria and South Africa) including fly ash from a South African coal combustion plant and the data obtained were used to elucidate similarities and differences between the studied coals. **Methods**- Moisture content, volatile matter, ash content and the Ultimate analysis of the samples were investigated. A comparative chemical analysis of South African Coal (SAC), Nigerian Coal (NGC) and the fly ash from SAC samples were individually investigated using these techniques: X-ray Fluorescence (XRF), Laser Ablation-Inductively Coupled Plasma Mass Spectroscopy (LA-ICPMS) and Fourier Transform Infra-Red Spectroscopy (FTIR). **Results**-The bulk chemical composition as determined by XRF showed high concentrations of SiO₂, Al₂O₃ in both SAC and NGC samples. The major oxides identified for the electric precipitated fly ash includes SiO₂, Al₂O₃, CaO, Fe₂O₃, MgO and TiO₂. Thirty seven (37) trace elements were analysed for in the samples with varying concentrations from 0 to over 100 mg/Kg. The SAC samples with concentrations greater than 100 mg/Kg in the SAC were Ba, Sr and As; and for NGC; As, Co, Zr, and W were identified. The trace elements in the fly ash which showed concentrations greater than 100 mg/Kg includes Ba, Ce, Sr, Zr, Cr and V. Enrichment of Co, Cr, Ni, Pb, Sb, Zn, U, Th and V was observed in the SAC fly ash analysed when compared with the source SAC sample, attesting to the relative higher relative densities of the metals. **Conclusions**-The SAC and NGC coals samples used in this study can be classified as medium volatile bituminous coal and a comparably low percentage ash was generated for the NGC and SAC samples. There is an indication of negligible amounts of sulphur in the samples.

Keywords: Nigerian coal, South African coal, Coal fly ash, Major oxides, Trace elements, Mineralogy.

1. INTRODUCTION

Coal is a combustible carbonaceous rock that contains varying amounts of carbon, hydrogen, nitrogen, oxygen, sulphur and mineral matter and nearly 8 gigatonnes per year of coal is produced globally at ~0.05 \$/kg [1]. It is an important energy resource, an organic rock that is composed of macerals and minerals and its reserves are abundant fuels necessarily needed to meet the demands of electricity [2]. The combustion of lignite, sub-bituminous, bituminous coal, and anthracite for power generation produces a range of coal combustion residues, also known as coal ash [3,4]. The growing interest in mineral matter and trace elements in coal and coal fly ash largely stems from environmental standards required for power generation.

According to Bergh et al. (2011) [5], South Africa is the 5th largest producer and joint 4th largest exporter of coal in the world. It is also a major supplier of coal to the European Union. It has the largest coal reserves in Africa at approximately 75% of Africa's total coal reserves, mining between 245 Mt to 250 Mt of coal per year and exporting around 71.4 Mt which is approximately a third of the total annual production [6,7] and sixth globally in economically recoverable coal reserves (34,224 Mt) and fifth in the world in annual production [8]. South Africa has an abundant coal reserve which is utilized in generating electricity and chemical production and in the process of its combustion generates about 40Mt of coal fly ash annually [9]. As much as 70% of the South African estimated coal reserve is located in the Waterberg, Witbank, and Highveld coalfields, as well as lesser amounts in the Ermelo, Free State and Springbok Flats coalfields [10]. South African coals are generally low in sulphur, nitrogen and phosphorus, and in the case of the first two, the contents are dependent on maceral composition and rank [11].

Nigeria equally has large coal reserves, estimated to be at least 2 billion metric tons of sub-bituminous to bituminous coals and unquantifiable lignite deposits with 650 million tonnes which are proven and spread over fifteen states [12]. Coal was the first commercial energy resource to be exploited in Nigeria. The fortune of coal exploration in Nigeria suffered greatly after the nation's independence, as the economy is mainly driven by crude oil exportation and local refining to date. Technological choice of diesel fuel for rail transportation and later to gas for electricity generation led to a decrease in coal production from almost 1 million metric tons in 1959 to less than 10 thousand tons in 2005 [13].

Nigerian coals are of cretaceous or early tertiary age and are mostly located in the eastern part of the country. They are mostly lignite and sub-bituminous, with some deposits of high volatile bituminous coal [14].

Coal combustion is usually accompanied with residual incombustible ash residue called fly ash and the coal properties impact the quality of coal combustion by-products (CCBs) [15]. Chemically, 90-99% of fly ash is composed of Si, Al, Fe, Ca, Mg, Na and K with Si and Al forming the major matrix [16]. These elements are found in the ash because of their high melting points and the short resident time the ash particles stay in the furnace during combustion. Carbon and nitrogen are oxidised into gaseous constituents during combustion; hence they are present in fly ash in negligible quantities. Fly ash varies from acidic to alkaline nature depending on the coal type and furnace temperature. Many studies have shown that the alkaline nature of most fly ashes from different power stations is as a result of some soluble basic oxides present such as CaO and MgO [17,18]. Trace elements in fly ash include As, B, Be, Cd, Co, Cr, Cu, Ga, La, Mn, Hg, Ni, Pb, Sc, Ag, tin, Sr, V, Y, Zn and Zr [19]. The average concentrations of most of these trace elements in fly ash are reported by El-Mogazi et al. (1988) [20].

The mineralogy of fly ash refers to both amorphous and crystalline phases and other mineral fractions in the fly ash. During combustion, the minerals in coal can become fluid (totally melted) or volatile, and may oxidise or undergo other gas phase reactions [21]. The rate of cooling in the post combustion zone determines if a particle is amorphous or acquires a crystalline structure [22,23]. If the mineral cools slowly, they can develop the characteristic crystalline structure. If cooling is rapid, they form spherical glassy particles. Certain trace elements such as HAP (Hazardous Air Pollutants) can have substantial implications, and the US Clean Air Act Amendments of 1990 specifically identified As, Be, Cd, Cr, Co, Hg, Mn, Ni, Pb, Sb, Se, and U as potential HAP's [5-15-24,25].

Even though coal is considered to have more environmental impacts than any other energy source, the relative scarcity of some valuable elements has prompted many companies to search for new mineral sources. Recently, prices of strategic minerals and rare earth elements have been rising dramatically due to global supply shortages and increasing demands [26]. In addition to new mining ventures and electronic recycling programs, coal ash has been suggested as a possible large untapped resource. It is well-known that coal ash contains many common metals (e.g., Al, As, Cr, Ni, Se) while some coal ashes also contain elevated concentrations of rare earth and strategic metals (e.g., Ce, La, Ga, Ge).

Several companies are already exploring methods to extract rare metals from coal ash and investigating whether coal ash processing can serve as an economical and environmentally friendly alternative to traditional mining [27]. Fly ash and bottom ash can be used in different industrial applications to minimise environmental impacts, for instance in ion-exchange (in industrial wastewater and soil contamination), and in the separation and removal of gases and solvents [28]. Relationship has been established on studies of trace element partitioning between chemistry of feed coal and fly ash. Further, a number of studies have demonstrated relationship between the collection point of the fly ash (electrostatic precipitator or baghouse row) and the concentration of trace elements [24].

The specific objective of the present study was to chemically, geochemically and mineralogically characterise coals from two contrasting environments (Nigeria and South Africa) as well as for the fly ash from a South African coal combustion plant. The data obtained were used to elucidate similarities and differences between the studied coals. The enrichment of the trace elements in the South African fly ash was equally determined and also used as a means of predicting the chemical composition and environmental impact expected for the future Nigerian coal fly ash.

2. MATERIALS AND METHODS

The feed coal at a large South African power station was sampled for 3 days during a field trip research activity. The sampling method employed was as described by Querol et al. (1994) [3] with slight modification. Every day, 20 kg of coal was obtained from a split of 2000t coal sampled throughout the day by means of an automatic sample-riffler located at the coal feeder of the boilers. After automatic homogenisation of the three samples, a gross sample of 60 kg was obtained. The coal combustion fly ash from the power station was also sampled simultaneously to compare their major and trace element content with that of the parent coal. Samples of 30 kg of the fly ash from the hoppers of the electrostatic precipitators in the same group were obtained. The gross coal sample was air-dried, milled and split carefully in accordance with ISO recommendations to obtain a representative 5 kg sub-sample of particle size < 250 µm for mineralogical and chemical analyses. The samples were tagged South African Coal (SAC) and fly ash (FA) respectively.

10 kg representative coal samples were batch wisely, randomly handpicked at five different locations in the Enugu coal preparation plant in Nigeria. The samples were reduced to smaller sizes by mechanical means, followed by pulverising in a rotary mill. The powdered samples were passed through a 210 micron sieve to prepare a representative 5 kg sub-sample for analysis. The sample was tagged Nigerian Coal (NGC).

The coals and fly ash samples were stored in sealed polyethylene sample bags and labelled accordingly. The sample bags were kept in a dark cool cupboard away from any source of heat, fluctuating temperature and direct sunlight to avoid contamination and oxidation as much as possible.

2.1 Proximate, Ultimate and Heating Value Analysis: Standard analytical procedures were used to investigate moisture content [29], volatile matter [30], ash content [31] and the Ultimate analysis [32]. Dulong formula [33] was used for the estimation of higher heating values (HHV) in MJ/kg for the SAC and NGC coal samples.

$$HHV(MJ/Kg) = 0.33801(C) + 1.44158 [(H) - 0.00125 (O)] + 94.13 (S) \quad (1)$$

Three (3) runs were undertaken on each sample to obtain the mean and standard deviation (SD). For calculating the energy released as (HHV) for coal samples, the breaking of C-C bonds was considered as the predominant source of energy released and negligible amount from sulphur linked bonds.

2.2 X-ray Fluorescence (XRF): X-ray fluorescence (XRF) spectrometry was used to determine the various metal oxides, including SiO₂, Al₂O₃, CaO, K₂O, Na₂O, Fe₂O₃, MnO, MgO, TiO₂, and P₂O₅, in the coal and coal ash samples. A Phillips PW1480 sequential X-ray fluorescence spectrometer was used. Samples were oven dried at 100°C for 12 hours to remove the absorbed water and then crushed with a mortar and pestle to fine powder. Nine grams of the dried powdered samples were mixed with 2g of binder (a mixture of wax C and EMU powder). Binders were used to glue the individual grains of the samples together before making the mixture into pellets at a pressure of 15 kbar for a minute. Loss on ignition (LOI) was measured by placing the samples in the furnace at 1000 °C for at least 45 minutes. To obtain the mean and standard (SD), three runs were undertaken on each sample.

2.3 Laser Ablation-Inductively Coupled Plasma Mass Spectroscopy (LA-ICPMS): Trace elements were analysed using ICP-MS (Agilent 7500ce). Samples were filtered with 45 µm membrane filter paper to remove suspended solids and refrigerated before LA-ICPMS analysis. The instruments were calibrated twice daily using multi-element standards, with calibration verification standard analysed directly after the calibration. The control standards for every 12 samples were run by the ICP-MS. Internal standards were used to correct for instrument drift in ICP-MS. The pressed pellet method was employed for trace element analysis. 8 ± 0.05 g of milled powder of each sample was mixed thoroughly with 3 drops of Mowiol wax binder, and pressed into pellet with Pill press to 15 ton pressure. They were then dried in oven at 100 °C for half an hour before analysing.

2.4 Fourier Transform Infra-Red Spectroscopy (FTIR): The FTIR analysis was carried out on a Perkin Elmer 100 series, Universal ATR accessory spectroscopy. This is for the purpose of identification and comparison of the functional groups present in each sample. Samples were oven dried at a temperature of 100 oC and crushed with mortar and pestle before analysis.

3. RESULTS

Table 1: The table presents proximate and ultimate analysis of coal samples.

	Mean	SAC S.D	C.V %	Mean	NGC S.D	C.V %
Nitrogen(N)%	1.16	0.17	14.3	1.65	0.24	14.3
Carbon (C) %	45.8	4.00	8.75	57.6	5.98	10.4
Hydrogen(H)%	3.50	0.41	11.8	4.90	0.34	6.97
Moisture%	0.78	0.33	42.5	0.81	0.19	23.3
Ash% (db)	9.44	2.25	2.38	9.32	1.31	1.40
Volatile matter(db)	5.58	2.25	40.31	6.80	1.31	19.2
C/N		39.5				34.9
H/C		0.08				0.09
HHV(MJ/kg)	20.526			26.533		

S.D: Standard Deviation; C.V: Coefficient of Variation; db: dry basis; HHV: Higher Heating Value.

Table 2: The table presents concentration of major oxides (weight %) in SAC and NGC samples as determined by XRF.

	Mean	SAC S.D	C.V	Mean	NGC S.D	C.V
Al ₂ O ₃	11.4	0.16	1.40	3.55	0.03	0.74
CaO	0.18	0.01	5.87	0.05	0.01	10.8
Fe ₂ O ₃	0.37	0.03	7.57	0.29	0.09	29.8
K ₂ O	0.62	0.01	1.47	0.06	0.01	8.66
MgO	0.12	0.01	4.22	0.06	0.01	8.66
MnO	0.01	0.00	0.00	0.01	0.00	0.00
Na ₂ O	0.14	0.00	2.44	0.14	0.00	3.44
P ₂ O ₅	0.28	0.01	1.90	0.02	0.00	0.00
SiO ₂	16.9	0.15	0.89	14.5	0.07	0.50
TiO ₂	0.44	0.01	2.08	0.47	0.01	1.12
LOI	67.9	0.16	0.23	79.9	0.54	0.67
H ₂ O-	2.44	0.20	8.01	1.33	0.69	29.5

Table 3: The table presents concentration of trace elements distribution in coal samples (mg/kg) as determined by LA-ICPMS as well as their comparisons with china, average U.S. and world coals.

Elements	NGC			SAC			USA ^b		world ^c	
	Mean	S.D	C.V%	Mean	S.D	C.V%	China ^a	Arithmetic		Geometric
As	403	9.84	2.44	231	18.4	7.96	3.79	24	6.5	8.3
Sc	4.37	0.18	4.02	9.32	0.53	5.69	4.38	4.2	3	3.9
V	32.2	0.54	1.69	54.7	1.57	2.88	35.1	22	17	25
Cr	36	2.4	6.66	53.2	1.79	3.36	15.4	15	10	16
Co	214	1.83	0.85	2.22	0.33	14.9	7.08	6.1	3.7	5.1
Ni	11.2	0.32	2.86	20.6	1.21	5.87	13.7	14	9	13
Cu	23.7	1.85	7.8	32.8	1.5	4.57	17.5	16	12	16
Zn	11.9	0.27	2.24	38.6	1.6	4.14	41.4	53	13	23
Rb	2.6	0.07	2.84	29.1	0.68	2.34	9.25	21	0.62	14
Sr	21	0.27	1.26	603	21.1	3.49	140	130	90	110
Y	5.74	0.07	1.19	16.8	0.39	2.32	18.2	8.5	6.6	8.4
Zr	151	2.39	1.58	96.6	2.04	2.11	89.5	27	19	36
Nb	8.18	0.01	0.14	10.4	0.8	7.67	9.44	2.9	1	3.7
Mo	1.77	0.01	0.33	3.48	0.3	8.64	3.08	3.3	1.2	2.2
Sn	1.69	0.16	9.3	3.48	0.24	6.77	2.11	1.3	0.001	1.1
Cs	0.24	0.01	2.63	5.72	0.24	4.23	1.13	1.1	0.7	1
Ba	46	0.54	1.17	1156	16.2	1.4	159	170	93	150
La	8.02	0.09	1.12	38.9	0.58	1.49	22.5	12	3.9	11
Ce	16.6	0.25	1.51	90.4	2.68	2.97	46.7	21	5.1	23
Pr	1.73	0.06	3.61	9.39	0.26	2.78	6.42	2.4	n.d	3.5
Nd	6.09	0.15	2.49	30	0.39	1.31	22.3	9.5	n.d	12
Sm	1.24	0.1	7.69	5.18	0.33	6.34	4.07	1.7	0.35	2
Eu	0.24	0.01	5.58	0.91	0.06	6.26	0.84	0.4	0.12	0.47
Gd	0.96	0.06	6.38	3.85	0.05	1.31	4.65	1.8	n.d	2.7
Tb	0.17	0.01	8.24	0.57	0.02	3.61	0.62	0.3	0.09	0.32
Dy	1.04	0.03	2.52	3.09	0.13	4.06	3.74	1.9	0.008	2.1
Ho	0.22	0.01	5.99	0.62	0.02	3.09	0.96	0.35	n.d	0.54
Er	0.66	0.06	9.41	1.86	0.11	6.05	1.79	1	0.002	0.93
Tm	0.1	0.01	9.42	0.27	0.02	5.59	0.64	0.15	n.d	0.31
Yb	0.75	0.03	4.49	1.76	0.14	7.74	2.08	0.95	n.d	1
Lu	0.12	0.01	8.94	0.26	0.02	8.49	0.38	0.14	0.06	0.2
Hf	3.87	0.07	1.81	2.75	0.07	2.36	3.71	0.73	0.04	1.2
Ta	0.56	0	0.52	0.84	0.06	6.74	0.62	0.22	0.02	0.28
W	1129	17.7	1.56	1.9	0.12	6.38	1.08	1	0.1	1.1
Pb	5.48	0.11	2.03	7.02	0.26	3.76	15.1	11	5	7.8
Th	4.19	0.09	2.08	14.2	0.42	2.95	5.84	3.2	1.7	3.3
U	1.42	0.05	3.66	3.87	0.17	4.27	2.43	2.1	1.1	2.4

Nd: no data; **a:** From [34-35]; **b:** From [36]; **c:** From [37].

Table 4: The table presents major oxides distribution in electric precipitated fly ash sample (EPFA) as determined by XRF.

Elements	Mean	S.D	C.V
Al ₂ O ₃	23.8	0.23	0.95
CaO	5.62	0.38	6.68
Fe ₂ O ₃	5.07	0.39	7.76
K ₂ O	0.71	0.17	23.5
MgO	1.41	0.25	18.1
MnO	0.05	0.01	12.4
Na ₂ O	0.27	0.21	76.6
P ₂ O ₅	0.32	0.23	70.4
SiO ₂	52.3	2.16	4.13
TiO ₂	1.41	0.01	0.82
LOI	7.70	1.40	18.2
H ₂ O-	1.17	0.64	54.8

EPFA: electric precipitated fly ash; LOI: loss on ignition.

Table 5: The table presents trace elements distribution in EPFA sample (mg/kg) as determined by LA-ICPMS.

Trace	Mean	S.D	C.V%
As	47.7	2.52	5.28
Sc	26.3	1.51	5.72
V	117	2.76	2.36
Cr	193	2.81	1.46
Co	16.8	0.41	2.44
Ni	50.2	1.88	3.73
Cu	32.3	3.37	10.4
Zn	53.6	2.68	4.99
Rb	37.1	0.81	2.19
Sr	1263	22.2	1.76
Y	64.9	0.37	0.57
Zr	393	1.48	0.38
Nb	35.0	1.28	3.66
Mo	5.80	0.24	4.18
Sn	6.68	0.34	5.10
Cs	5.85	0.16	2.74
Ba	1057	9.57	0.90
La	90.8	0.76	0.84
Ce	180	2.76	1.53
Pr	19.5	0.39	2.00
Nd	71.2	1.26	1.77
Sm	14.4	0.39	2.69
Eu	2.71	0.13	4.62
Gd	12.4	0.26	2.08
Tb	1.94	0.01	0.52
Dy	11.9	0.31	2.60
Ho	2.38	0.08	3.37
Er	6.56	0.03	0.49
Tm	0.96	0.05	5.20
Yb	6.36	0.17	2.67
Lu	0.92	0.10	11.2
Hf	10.6	0.51	4.85
Ta	2.67	0.05	1.98
W	5.74	0.07	1.22
Pb	34.7	0.51	1.47
Th	36.2	0.36	1.01
U	10.0	0.21	2.13

Table 6: The table presents predicted Enrichment factors (EF) for trace elements in fly ash from coal with and without normalization to Ce (mg/kg).

	SAC	EPFA	EF _{Ce}	EF _{Dv}
As	231	47.7	0.10	0.21
Sc	9.32	26.3	1.42	2.82
V	54.7	117	1.07	2.14
Cr	53.2	193	1.82	3.63
Co	2.22	16.8	3.80	7.57
Ni	20.6	50.2	1.22	2.44
Cu	32.8	32.3	0.49	0.98
Zn	38.6	53.6	0.70	1.39
Rb	29.1	37.1	0.64	1.27
Sr	603	1263	1.05	2.09
Y	16.8	64.9	1.94	3.86
Zr	96.6	393	2.04	4.07
Nb	10.4	35.0	1.69	3.37
Mo	3.48	5.80	0.84	1.67
Sn	3.48	6.68	0.96	1.92
Cs	5.72	5.85	0.51	1.02
Ba	1156	1057	0.46	0.91
La	38.9	90.8	1.17	2.33
Ce	90.4	180	1.00	1.99
Pr	9.39	19.5	1.04	2.08
Nd	30.0	71.2	1.19	2.37
Sm	5.18	14.4	1.40	2.78

Eu	0.91	2.71	1.50	2.98
Gd	3.85	12.4	1.62	3.22
Tb	0.57	1.94	1.71	3.40
Dy	3.09	11.9	1.93	3.85
Ho	0.62	2.38	1.93	3.84
Er	1.86	6.36	1.72	3.42
Tm	0.27	0.96	1.79	3.56
Yb	1.76	6.36	1.81	3.61
Lu	0.26	0.92	1.78	3.54
Hf	2.75	10.6	1.94	3.85
Ta	0.84	2.67	1.60	3.18
W	1.90	5.74	1.52	3.02
Pb	7.02	34.7	2.48	4.94
Th	14.2	36.2	1.28	2.55
U	3.87	10.0	1.30	2.58

DV: Direct value computed without reference to Ce.

Table 7: The table presents projection for trace elements in NGC fly ash (mg/kg).

Trace	NGC	Projection for NGC fly ash	
		EF _{DV}	
As	403	0.21	83.2
Sc	4.37	2.82	12.3
V	32.2	2.14	68.9
Cr	36.0	3.63	130
Co	214	7.57	1619
Ni	11.2	2.44	27.3
Cu	23.7	0.98	23.4
Zn	11.9	1.39	16.5
Rb	2.6.0	1.27	3.31
Sr	21.0	2.09	44.0
Y	5.74	3.86	22.2
Zr	151	4.07	614
Nb	8.18	3.37	27.5
Mo	1.77	1.67	2.95
Sn	1.69	1.92	3.24
Cs	0.24	1.02	0.25
Ba	46.0	0.91	42.1
La	8.02	2.33	18.7
Ce	16.6	1.99	33.1
Pr	1.73	2.08	3.59
Nd	6.09	2.37	14.5
Sm	1.24	2.78	3.45
Eu	0.24	2.98	0.71
Gd	0.96	3.22	3.09
Tb	0.17	3.40	0.58
Dy	1.04	3.85	4.01
Ho	0.22	3.84	0.84
Er	0.66	3.42	2.26
Tm	0.10	3.56	0.36
Yb	0.75	3.61	2.71
Lu	0.12	3.54	0.42
Hf	3.87	3.85	14.9
Ta	0.56	3.18	1.78
W	1129	3.02	3410
Pb	5.48	4.94	27.1
Th	4.19	2.55	10.7
U	1.42	2.58	3.67

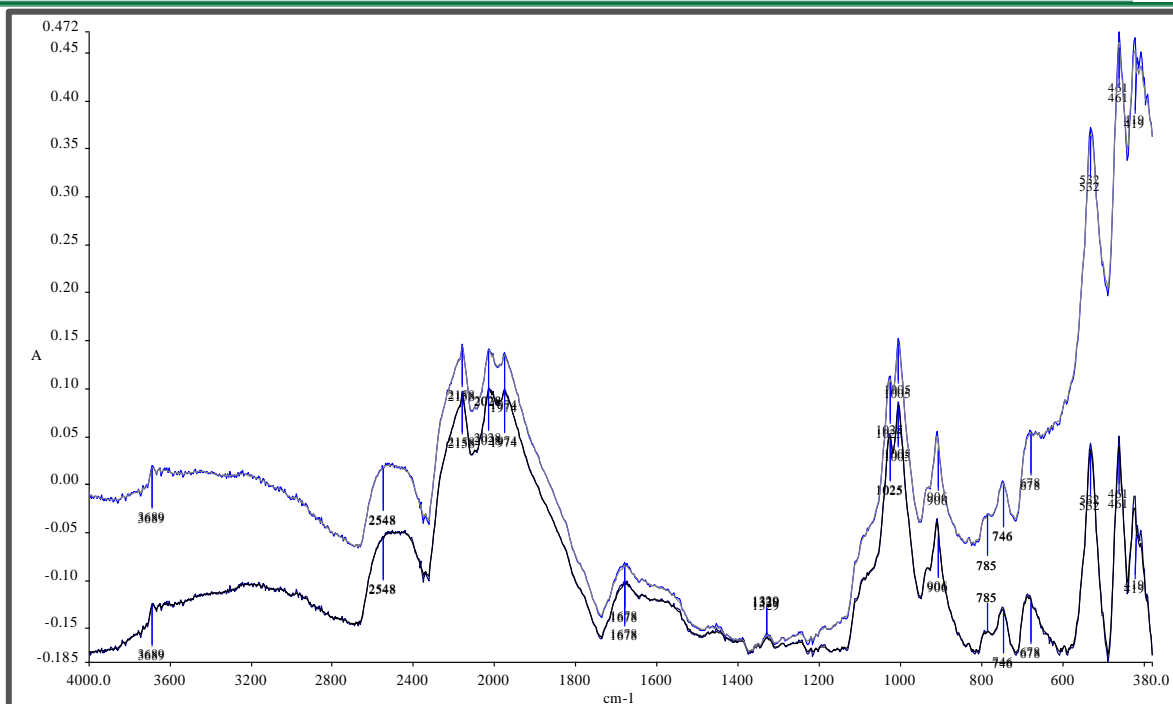


Figure 1: The figure presents FTIR spectra for Nigerian coal sample.

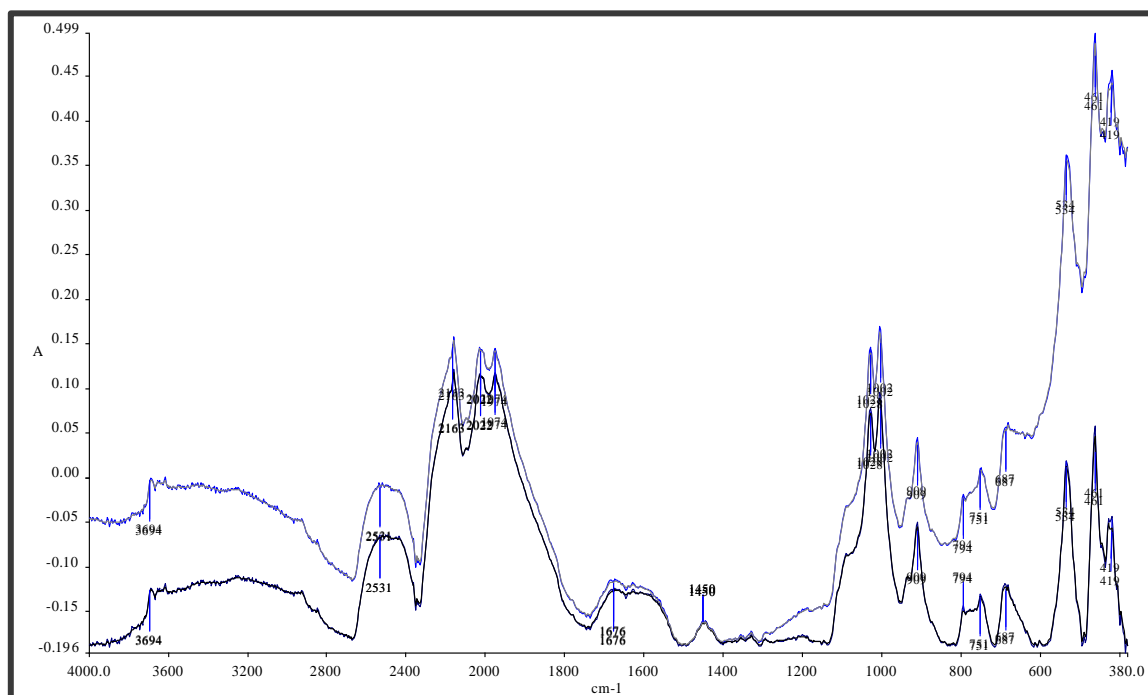


Figure 2: The figure presents FTIR spectra for South African coal sample.

4. DISCUSSION

Proximate and Ultimate Analysis of coal samples

Proximate analysis gives the weight fraction of moisture, volatile matter (VM) including liquids and tar, fixed carbon (FC), and ash, according to ASTM standard test method E870-82 [38]. The average fixed carbon contents of NGC and SAC are $57.6 \pm 5.98\%$ and $45.8 \pm 4.00\%$ with coefficient of variation of 10.4% and 8.75% respectively as presented in Table 1. The NGC data shows slightly higher fixed carbon content than the SAC data. The fixed carbon content is a measure of the solid combustible material that remains after the volatile matter in coal has been removed. The ultimate analysis indicates average hydrogen contents of NGC and SAC samples as $4.90\% \pm 0.34$ and $3.50\% \pm 0.41$ with coefficient of variation of 6.97 and 11.8 respectively while the nitrogen values of NGC and SAC are $1.65\% \pm 0.24$ and $1.16\% \pm 0.17$ with coefficient of variation of 14.3% and 14.3 % respectively. The result indicated a low nitrogen and hydrogen contents for the two samples and an increase in the carbon content. The obtained values for C, N and H contents in SAC are within the range of reported proximate values for South African coals [39,40]. The lower H/C ratio for SAC sample indicates that it is likely to be more aromatic than the NGC sample [39].

The average ash contents (dry basis-db) of the NGC and SAC are 9.32 ± 1.31 % and 9.44 ± 2.25 with coefficient of variation of 1.40% and 2.38 % respectively indicating marginal low ash content in NGC than the SAC. These values are slightly higher but comparable to those of Nigerian sub-bituminous coals reported by Aswen (1987) [41] with values for Okaba, Benue (5.30 %) and for Obi, MB Benue (5.80%). The SAC (9.44 %) and NGC (9.32 %) values are however higher than the Polish coals (4.79 %) and the American coal (5.77 %). High ash yields are obtained from coals that are generally found to be intimately mixed with fairly large proportion of mineral matter [42-44]. The ash content values of these coals are generally minimal. The NGC and SAC samples investigated have average volatile matter (db) contents of 6.80 ± 1.31 % and 5.58 ± 2.25 % with coefficient of variation of 19.2% and 40.3% respectively. This low VM could be due to maturity influence because volatile matter is known to decrease with increase in rank [45], therefore, coals with this VM content is a high rank coal.

The VM values indicate a high carbonaceous material even though the volatile matters of some Nigerian coals are Chikala coal (44.27%), Lafia-Obi (29.39%); the American coal (31.36%) and the Polish coal (32.61%). Nasirudeen, Jauro (2011) [46] study confirmed that a large and significant difference can exist with studied coals. We also compared our findings with the study of five characterised black Australian bituminous coals [47], the moisture content, ash and fixed carbon are similar and comparable, however, the volatile matter range of (19.68 - 45.41) of the Australian coals were still a lot higher than SAC (5.58) and NGC (6.80). This affirms that the volatile matter of the NGC and SAC coal sample used in this study are considerably very low. Volatile matter is used in coal ranking and one of the most important parameters used for determination of coal's applications [48]. Volatile matter does not form part of the coal; it is usually evolved as tar during carbonisation. High-volatile bituminous coal due to its high volatile matter content generates high pressure during carbonisation [49,50], therefore the SAC and NGC are expected to comparatively generate average pressure during carbonisation.

The average value of the moisture content for NGC and SAC samples are 0.81 ± 0.19 and 0.78 ± 0.33 % with coefficient of variation of 23.3% and 42.5% respectively. Aswen (1987) [41] reported a higher moisture values for Nigerian coals in Okaba, Benue (3.50%) and Obi, Benue (3.45%), indicating that the values are slightly higher than the values obtained in this study. Considering the coals' moisture contents, a higher quality coal has low moisture. High moisture leads to a decrease plant capacity and an increase in its operating costs, by affecting the calorific value and the concentration of other constituents [48]. The total moisture content is important in assessing and controlling the commercial processing of coal. The present values suggested that these samples will require less heat for vaporisation of the moisture.

This result also indicate a good calorific values for the coal samples with the NGC (26.533 MJ/kg) having a slightly higher heating value when compared with the SAC (20.526 MJ/kg). Relatively low value of moisture content represents a significant improvement in coal's quality because moisture affects the calorific value and the concentration of other constituents [46]. The heating value is one of the most important properties of fuels for design calculations or numerical simulations of thermal conversion systems [51]. The chemical properties of these coals show low values for moisture contents, ash and volatile matter as expected with the views held by Gray, Barrass et al., (1979) [52] except the volatile matter content. The coal used in this study can be classified as medium volatile bituminous coal according to ASTM specification [53].

Bulk chemical and major element composition of the coal samples

The elemental composition of the coal samples determined by XRF for the samples is presented in Tables 2 and 3 and it presents major elements as oxides (weight %) and traces in (mg/kg) on a dry weight basis. The most abundant oxide constituent in both coals was SiO_2 with about (16.9%) for SAC and (14.5%) for NGC. This is closely followed by Al_2O_3 (11.4%) for SAC and (3.55%) for NGC.

It was observed that Al_2O_3 in NGC was very low compared with SAC but the SiO_2 in both samples was however relatively close. Table 2 also revealed that the loss on ignition (LOI) (79.9%) is higher in NGC than in SAC with LOI (67.9%) while MnO (0.01), Na_2O (0.14) were similar in the samples analysed. In pyro-processing and the mineral industries such as lime, calcined bauxite, refractories or cement manufacture, the loss on ignition of the raw material is roughly equivalent to the loss in mass that it will undergo in a kiln, furnace or smelter.

High levels of sodium found in many low-rank coals have been found to be responsible for fouling in the combustion chambers [54,55]. There would be less fouling in combustion chambers for the combustion of SAC and NGC samples due to the content of sodium present. The concentrations of acidic oxides of Si, Al and Fe are generally high in the two samples while the comparative concentrations of basic oxides of Mg, Ca, Na and K are lower, this suggests that there would be a low level of base neutralising cations for the samples. Similar observations and conclusions have been made by Ehinola, Adene (2008) [56] in his study.

The SAC samples contain higher concentrations of some typical radioactive elements such as Ba (1,156 mg/kg), Rb (29.1 mg/kg), U (3.87 mg/kg), Sr (603 mg/kg) and Th (14.2 mg/kg) when compared to the analysed NGC sample with Ba (46.0 mg/kg), Rb (2.60 mg/kg), U (1.42 mg/kg), Sr (21.0 mg/kg) and Th (4.19 mg/kg). This low concentration of elements indicate fewer introductions of radioactive elements on the natural environment for the NGC however, the significant presence of some quantities of elements could also be an alternative source of strategic minerals and rare earth elements which have risen dramatically due to global supply shortages and increasing demands.

It is common knowledge that trace elements in coals are both inorganically (the greatest part of them) and organically associated [36-57-59]. The concentrations of most trace elements in SAC and NGC studied in this work are similar and comparable to China, US and world coals reported [34-37]. However, NGC have higher content of As, Co, Zr and W and SAC showed high contents of As, V, Sr, Zr, Nb, Ba, Ce than the china, US and world coals. Recent study have posited the possibility of removing volatile trace elements prior to combustion may be an attractive emission control method which is likely to be less expensive than post-combustion clean up, and may well prove to be more effective where the trace elements are able to pass through pollution control devices [60]. Studies has also shown that the elemental concentrations of in situ coal seams can vary both vertically and laterally, even between coals in a mine, from different mines or between coals from the same seam in various location of a mine or a coal bearing strata [61].

The sum of the mean electric precipitated fly ash sample values of SiO_2 , Al_2O_3 , and Fe_2O_3 was 81.17%. This electric precipitated fly ash can be classified as class F [62] having a percentage aggregates sum of alumina, silica and ferric oxide contents greater than 70 %, with a lime content less than 10%. The present result confirmed that the fly ash is derived from the burning of bituminous coal. The main inorganic elements observed in the electric precipitated fly ash as revealed by XRF are Si and Al, suggesting abundance of quartz and aluminosilicate minerals in the coal sample. CaO (5.62 %) and MgO (1.41 %) are basic oxides which when dissolved in aqueous solution could lead to an increase in the pH of the fly ash solution, while the Fe_2O_3 (5.07 %) which is an acidic oxide could decrease the pH of the fly ash solution when dissolved in aqueous solution. All the major elements were enriched in the SAC except K_2O and P_2O_5 .

This is not unexpected since coal fly ash particles either adsorb elements on their surface or trap them in the glass aluminosilicate fraction. Therefore, the slow dissolution of the glass fraction upon hydration may be responsible for the slow release of elements like Mn, Si, K and P [17]. Loss on Ignition (LOI) of the electric precipitated fly ash sample is one of the most important chemical properties of fly ash especially since it is an indicator of the fly ash's suitability for use as a cement replacement in concrete. The electric precipitated ash sample has a low LOI (7.70 %) when compared with the parent coal (SAC) with (67.92%) indicating that most of the volatile components of this fly ash had already been devolatilized. The diversity of the results of these studies may be directly attributable to the coal sources because of their different element distributions [63].

Trace elements originating from coal utilisation that are believed to be of major concern from a human health perspective include: As, Cd, Hg, Pb, and Se [64]. However, fly ash derived from combustion of coals may also have potential economic significance especially for rare metals [65,66]. The studied fly ash showed Co, Nb, Ni, Pb, V, Zr and U have highly-elevated concentrations in the electric precipitated fly ash than the parent coal (SAC), and this is probably due to the evaporation of these metals in combustion chambers which are being disposed off in the gaseous product. In comparison, As, Ba, Ce, Rb, Sr, Y, and Th are the elements with higher concentrations in the parent South African coal (SAC) sample.

It is common knowledge that trace elements in coals are both inorganically (the greatest part of them) and organically associated [36-57-67], rare earth elements in coal appear to consist of a primary fraction which is associated with syngenetic mineral matter [68]. Another portion of the REE can be externally derived or mobilised when primary mineral matter is destroyed or modified [69]. Although REEs are not considered to be highly mobile in low-temperature environments, some researchers have suggested possible mechanisms for mobilising REEs in coal [70]. Therefore, the REEs could be bound to the surfaces of clay minerals, and may be retained in highly resistant REEs-rich trace minerals.

It has been reported that elements in coal fly ash are dependent on the characteristics of the coal burned, combustion conditions and removal efficiency of air pollution control device. Coal combustion by-products are constantly changing, partly due to variations in coal sources, and the constant need to use the ash collection system as part of the gaseous emission-control system [24]. Generally, toxic elements such as As, Ba, Cr, Ni, Sb are released either with particles or as vapours [71]. The observed increased concentration of these metals with the ash yield suggests a high affinity to the inorganic matter [72]. The present results show that most trace elements are enriched in the ash, except for As, Ba, Lu, which show a significant decrease. These results confirmed earlier studies by Pires and Querol 2004 [73], which suggested a volatile nature for most of these elements [74] at high combustion

temperatures (1400 – 1600 °C) followed by condensation on the fly ash particle surface. Cu and Cs are distributed evenly within the coal (SAC) and electric precipitated fly ash.

FTIR analysis of coal samples

The different chemical bonding present in the coal samples were determined using the FTIR procedure. Figures 1 and 2 present the FTIR spectra for the NGC and SAC and the coals spectra shown are broadly similar and show characteristic vibration bands of the coal. In assigning the bands, the absorption bands are compared with the standard patterns [2-75, 76]. It is known that the 900 – 700 cm^{-1} region corresponds to aromatics bending modes, 1450 cm^{-1} and 1380 cm^{-1} bands correspond to aliphatic bending modes, and 2800–3100 cm^{-1} region corresponds to aliphatic and aromatics stretching modes [77]. The elements in coal can occur in a wide variety of chemical forms or modes of occurrence. It is important to emphasise that it is the mode of occurrence of an element that dictates its behaviour and its technological, environmental and economic impact [36]. The modes of occurrence of the potentially hazardous elements in coal will be of significance in any attempt to reduce their mobilisation due to coal combustion [78].

Most of the peaks in FTIR spectra of coals between 1100 cm^{-1} and 400 cm^{-1} can be assigned to clay minerals such as quartz, kaolinite, illite and the montmorillonite group. Distinct peaks at the regions of 1000, 529 and 413 cm^{-1} are ascribed to kaolinite [79]. In kaolinite, the high frequency OH vibrations occur at the region of 3600 cm^{-1} while Si-O bending vibrations contribute to the strong absorption at 413 and 529 cm^{-1} . The presence of quartz in the coal sample possibly gives rise to the IR spectrum with absorption frequency at 746 and 684 cm^{-1} in the coal samples [80-82]. A strong absorption at 1025 cm^{-1} in the FTIR of NGC coal and 1028 cm^{-1} in SAC coal can also be ascribed to the presence of the mineral quartz. The potassium selenium chlorides also absorb at 1625 and 1450 cm^{-1} . The small shoulder at 1450 cm^{-1} in SAC could be attributed to potassium selenium chlorides.

The most relevant signals on the FTIR spectrum for coals are the absorption bands in the region between 850 and 650 cm^{-1} . The bands near to 840, 805 and 780 cm^{-1} are attributed to AlO_4 groups; the bands around 720, 685, 640 and 570 cm^{-1} are ascribed to AlO_6 groups. At low frequencies, under 400 cm^{-1} , absorption bands are caused by Ca-O bonds [83, 84]. The sampled coals are more of the AlO_4 groups. The spectra indicated that the coal sample used in the present study had little iron sulphide. The iron sulphide (pyrite) is generally the most important of the iron-bearing minerals in coals (basic absorption frequency at 413 cm^{-1}) which is missing in the NGC and SAC. This is an indication of negligible amounts of sulphur in the samples.

A broad absorption band is observed at 3689 cm^{-1} in the NGC and 3694 cm^{-1} in the SAC, which is mainly due to N-H and O-H groups. The peaks for O-H stretching vibrations at 3689 cm^{-1} for NGC and 3694 cm^{-1} for SAC appear to be for those associated with clay minerals. The aromatic hydrogen band at 3040 cm^{-1} is absent in the coals indicating its highly substituted and condensed nature [85]. The C-H stretching vibration peak at 2548 cm^{-1} for NGC and 2531 cm^{-1} for SAC, appearing as sharp peaks of medium intensity may be assigned to aliphatic and alicyclic CH_3 , CH_2 and CH groups although the major contribution is expected to be due to CH_2 groups. From this investigation, the major mineral identified in NGC is kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and quartz (SiO_2) while the FTIR spectra of SAC revealed potassium selenium chloride (K_2SeCl_6), quartz (SiO_2) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) as the major crystalline mineral phases present. The spectra of the SAC and NGC samples are very similar, therefore this present results show that NGC and SAC are found to be similar in mineralogical compositions using the FTIR analyses.

Enrichment factors of the trace elements

The distribution of trace elements in coals used for electrical generation is of increasing importance in the assessment of environmental impacts from coal-fired power plants [86]. To elucidate the behaviour of the trace elements during the coal combustion and to gauge the extent of anthropogenic influence, their concentrations in fly ashes can be normalised using a non-volatile element, whose concentrations both in the coal and in the ashes are accurately known. This enrichment factor (EF) [87-89] was calculated as shown below:

$$EF = [(X_{Ash})/(Y_{Ash}) / (X_{Coal})/Y_{Coal}] \quad (2)$$

Where $[X]_{Ash}$ and $[X]_{Coal}$ are the concentrations of the X element in the fly ash and in the coal respectively. $[Y]_{Ash}$ and $[Y]_{Coal}$ are the contents of a non-volatile element taken as reference. The non-volatile elements most frequently selected for calculation of EF are Al, Ce, Fe, La, Si and Ti [90]. Most heavy rare earth elements (REEs) such as Ce and La present the additional advantage of being present in constant concentrations in all particle sizes of the fly ashes. Consequently, Ce was chosen as the reference element in the calculation of the enrichment indices of elements. The enrichment factor without Ce i.e direct values (DV) was also calculated; here the SAC data were normalised with that of the electric precipitated fly ash using this equation:

$$\text{Enrichment/Depletion (DV)} = \frac{\text{wt \% of element in the EPFA}}{\text{wt \% of the element in SAC}} \quad (3)$$

The results showing the Ce-normalised EF for studied elements, calculated for the fly ashes in relation to Ce and without Ce are presented in Table 6. The values below 1.0 represent relative enrichment in the coal sample while values above 1.0 represent relative enrichment in the fly ash sample. Co (3.80) and Pb (2.48) appeared to be the most volatile radionuclide measured due to its volatilisation and later condensation in the fly ash matrix since heterogeneous condensation is a surface-area phenomenon. A comparison of the results of assessment of enrichment factors obtained by the two methods demonstrates that EF_{Ce} indicate much lower value than the EF_{DV} factors.

Trace elements such as Zn, Rb, Cs, Mo and Sn are slightly enriched in the coal ash. The slight enrichment of these trace elements in the coal ash is attributed to the combustion process. On the contrary, only As, Cu and Ba is considerably depleted in the coal ash samples used in the present study. Rare earth elements (REEs) such as Ce, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Hf are slightly enriched in the coal ash. In summary, most of the determined trace and REE elements were comparatively enriched in the coal ash when compared with the parent material (coal) indicating an increased mobilisation of trace elements. The calculated trace element enrichment factors result showed that for the trace elements analysed, enrichment factors were higher for the fly ash, a finding that indicates that greater elements migrated into the fly ash and a volatile behaviour for the trace elements.

It is evident from the results that most elements exhibit moderate to significant enrichment in the coal fly ash. This enrichment of REEs in the coal ash result trend shows agreement with the previous work on the South African coal and combustion products [39-91], but disagreed with the held views of Baioumy (2009) [69] and Swaine, (2013) [58]. The trace and REE elements relative enrichment in coal ash is attributed to the combustion process in the Tutuka power station. Rare earth elements in coal appear to consist of a primary fraction which is associated with syngenetic mineral matter [68] and another portion of the REE can be externally derived or mobilized when primary mineral matter is destroyed or modified.

Prediction of chemical composition of Nigerian coal fly ash

Several studies on the occurrence and distribution of trace elements in coal have shown that their affinities differ from one deposit to another [92,93]. However, using insight from South African coal fly ash, a forecast of the pattern of enrichment and depletion factors of trace elements of Nigerian coal fly ash could be made when large scale coal processing may commence in Nigeria. Table 7 below shows the predicted composition of trace elements in the Nigerian coal fly ash using the enrichment factor obtained for each element in the SAC (Table 6). Enrichment in most elements that deserve particular interest from the environmental and human health point of view will be revealed when compared with the element concentrations in the feed coal.

The predicted content of NGC fly ash will likely contain trace elements like Sc, V, Cr, Ni, Zn, Rb, Sr, Y, Zr, Nb, Mo, Sn, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Pb, Th, U, and metal oxides such as Al_2O_3 , CaO , Cr_2O_3 , Fe_2O_3 , K_2O , MgO , MnO , Na_2O , P_2O_5 , SiO_2 , TiO_2 suggesting a predominantly volatile nature for these elements at high combustion temperatures followed by condensation on the fly ash particle surface. In contrast, Zn, Rb, Cs, Mo and Sn will be distributed evenly within the ash and NGC feed coal while As, Cu and Ba will show depleted concentration in the fly ash samples (Table 7).

The mineralogical composition of SAC and NGC coals includes kaolinite and quartz. As it was revealed for the SAC fly ash, the NGC fly ash will likely be composed of mullite, quartz, calcite, magnetite, and hematite minerals from the parent coal. Analyses of major elements from NGC fly ashes indicate a high amount of SiO_2 , Al_2O_3 , and Fe_2O_3 and similar pattern is revealed for the SAC fly ash. The low-calcium class F fly ash will be produced from the burning of NGC coal.

5. CONCLUSIONS

It has been shown that there is very high similarity between the SAC and NGC samples. This work gave us an understanding of coal quality characteristics in SAC and NGC and their fly ash. The Information on the concentrations and distributions of major and trace elements in coal and coal fly ash in SAC, their modes of occurrence, and the textural relations of the minerals and the organic components in which they occur may help to anticipate the behaviour of the major and trace elements during coal combustion for the NGC fly ash.

- The SAC and NGC coals samples used in this study can be classified as medium volatile bituminous coal
- The NGC and SAC samples have an estimated high heating value of 26.53 MJ/kg and 20.53 MJ/kg respectively which are high calorific value coals.
- XRF analyses revealed the main constituents of the electric precipitated fly ash samples to be SiO_2 , Fe_2O_3 and Al_2O_3 indicating the abundance of quartz and aluminosilicate minerals in the coal sample.
- Most elements exhibit moderate to significant enrichment in the coal fly ash

- It can be predicted that the NGC fly ash is likely going to be similar in composition to that of SAC fly ash mineral phase. Analyses of major elements from NGC coal fly ashes would also indicate a high amount of SiO₂, Al₂O₃, and Fe₂O₃.
- A comparably low percentage ash will be generated for the NGC and SAC samples.

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