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NIGERIAN COAL ANALYSIS BY PIXE AND HEBS TECHNIQUES *

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ABSTRACT

PIXE and HEBS techniques were employed for the measurement of the concentrations of the major, minor and trace elements in Nigerian Coal samples from a major deposit. The samples were irradiated with 2.55 MeV protons from the 3 MeV tandem accelerator (NEC 3 UDH) in Lund. The PIXE results are reported and compared with an earlier work on Nigerian Coal using FNAA and INAA analytical techniques while the HEBS results are compared with ASTM previous results. The results corroborate the assertion that Nigerian coals are of weak and noncoking grades with low sulphur of (0.82-0.99)% and relatively high hydrogen (4.49-5.16)% contents. The motivation for this work is partly due to the projected usage of coal as metallurgical feedstocks and as fuel, and partly because of the genuine concern about the concomitant environmental effects of the increased burning of coal. The knowledge of the concentration of all elements is important for the characterization of coal and the determination and control of its products. Economic parameters such as the ash contents and calorific values are associated with the concentrations of coal's constituents.

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1. Introduction

Since the discovery of coal in Nigeria in 1909, and the subsequent mining at Obwetti in Enugu in 1916, there has been some milestone in the development and expansion of coal geared towards its maximum utilization. Consequently, the Nigerian Coal Corporation (NCC) was recently saddled with four principal responsibilities namely [1], to supply coal requirements of the Ajaokuta steel plants as blend to the imported coking coal, to increase coal supply to the Nigerian cement works, to meet coal demand of the proposed 1,300 MW coal-fired power stations and lastly to produce enough coal for Nigerian Railway Corporation, small industries, domestic consumers and for the export market. Apart from these cardinal objectives, the by-products of coal such as tar and fertilisers which are presently imported, add incentives to the development of Nigerian coals.

At present, Nigerian coals are located in Enugu, Ezimo, Orukpa, Okaba, Ogboyoga, Inyi, Asaba and Lafia-Obi. The proven reserves in the aforementioned areas totalled about 640 million tons and the inferred reserves about a billion tons. They comprise of bituminous, sub-bituminous, lignitic and coking coals. Nigerian lignitic coals have high calorific values (about 5,000 Kcals/Kg) [1]. This qualifies them for power generation and heat raising. Besides, the lignites are known to be very rich in hydrocarborns, waxes and resins. This makes them suitable for the production of liquid fuels and chemicals.

The domestic coal demand presently are to the tune of 4 million tons annually. Preparation is at the top gear to build a number of coal-based power plants. The estimated demand from Nigeria National Electric Power Authority (NEPA) alone is about 4 million tons by the year 1990, and is expected to rise in subsequent years. This projected use of coal both as fuel and as metallurgical feedstocks in Nigeria Iron and Steel Industry has naturally led to a genuine concern about the concomitant environmental effects of the increased burning of coal. For instance, it is important to analyse the concentrations of elements such as sulphur for pollution control and chlorine to prevent boiler erosion [2]. Information about the elemental concentrations of Nigerian coals therefore becomes important for its characterization as well as determination and control of the quality of its product. Coal is essentially made of three components, the combustible elements ($Z \approx 6$), the mineral elements ($Z \simeq 12$) and water. There is a correlation between the mineral contents of the raw coal and the ash content after incineration [3]. Thus, economic parameters such as the ash contents and calorific values are associated with the concentrations of coals' constituents. In addition, the variation in elemental concentrations could be an indicator to the geochemical, geological and geographic histories of various deposits.

Over the years, and for various applications, a whole horizon of nuclear analytical techniques have become the arsenal for assaying elemental concentrations of various samples. Particle Induced X-ray Emission (PIXE) technique in particular seems to have climbed high on the ladder of success. The spectrum of applications include Medicine,

especially Haematology and Oncology, Biology, Geology, Mineralogy, Metallurgy and Material Science Studies, Criminology, Environmental Studies (aerosol studies), pollution control, Archaeology, etc to name a few. In this work, PIXE and High Energy Backscattering (HEBS) complementary techniques were employed for the measurement of concentrations of the major, minor and trace elements in Nigerian coal samples from Enugu deposit which is a major and the oldest deposit in Nigeria.

Enugu coals are sub-bituminous. Hannan et al [4] have shown that Nigerian coals are mostly sub-bituminous. Thus Enugu coal is a representative of a larger percentage of coals in Nigeria. Enugu raw coal has a gross calorific value of 5,935 K cal/Kg while the gross calorific value of its d.a.b. is 8,070 Kcal/Kg.

PIXE technique was employed for the determination of the concentrations of minor and trace elements, while HEBS technique was used to obtain the concentrations of the major elements. The PIXE results are reported and compared with an earlier work by Borishade et al [5] and Hannan et al [4] on Nigerian Coals using Fast Neutron Activation Analysis (FNAA) and Instrumental Neutron Activation Analysis (INAA) techniques; while the HEBS results are compared with American Society of Testing and Materials (ASTM) previous results.

2. Experimental method

2.1 Sample preparation

For PIXE measurements, the twenty four samples were cut and ground into powder form, then pellets were made out of

them using a special machine designed for it. They were then mounted on slide frames ready for irradiation. However, for HEBS measurements, four coal samples were cut with a diamond saw, the surfaces were then first polished with a coarse "emery-cloth", then polished fine (800 mesh). They were later dry polished with aluminum oxide (1000 mesh) on a paper lying on a glass surface until the surfaces became very smooth and there were no scratches on them. The other surface of the samples were then cut with a diamond saw and glued with two-component glue on glass plates. The samples were then polished with 200 mesh/800 mesh "emery-cloth" until each thickness, measured using micrometer gauge, was 20μm thicker than that desired. The four samples were then machine polished with 6μm and 1μm abrasive paste and mounted on slide frames for irradiation. The samples were between 40-100μm thick.

2.2 Sample Irradiation

The measurements were performed using 2.55 MeV protons from the 3MV electrostatic tandem accelerator (Pelletron 3 UDH) in Lund, Sweden. The target chamber is specially designed to take 40 samples mounted on slide frames with automatic sample changing device in vacuum. This set up, dedicated for routine PIXE analysis, has been calibrated using 33 different thin standards from Micro Matter Co [6]. Please see refs [7] and [8] for detailed description.

X-rays produced were detected in an internally collimated 80mm^2 Si(Li) Kevex detector. The detector has a 25μm beryllium window, a gold contact of 40μg/cm^2 and a silicon dead-layer of 70μg/cm^2[[6]. Its energy resolution was 158eV at 5.9 KeV. The backscattered protons were detected in a silicon surface

barrier detector. The standards used were Kapton(R) foil, a polyimide film, $C_{22}H_{10}N_2O_5$ and Mylar(R) foil, a polyester film, $C_{10}H_8O_4$.

2.3 Data Analysis

The height of an energy spectrum for a compound sample containing more than one element is given as [9]

$$H_{A,O} = \sigma_A(Eo)\,\Omega\,Q\,\frac{C_A}{M_A.U}\,.\,\mathcal{E}\,.\,\frac{1}{\left\{K_A\frac{dE}{dx}\Big|_{Eo} + G\frac{dE}{dx}\Big|_{K_AE_o}\right\}} \qquad (1)$$

where σ_A (Eo) is the average differential scattering cross section between the projectile and the sample evaluated at the incident energy Eo, Ω the solid angle spanned by the detector aperture, Q the total number of incident protons bombarding the sample, $\mathcal{E}$ the energy width of a channel determined by the electronic setting of the detecting system, C_A concentration of element A, M_A atomic mass of element A, $U = 1.6603 \times 10^{-27}$ Kg, G the geometrical factor, K_A the Kinematic factor, $\frac{dE}{dx}\Big|_E$ is the stopping power evaluated at energy E.

Comparison of coals results with those of the standards Kapton and Mylar simplifies equation (1) and makes the evaluation of the major elemental compositions of coal possible. The mass fractions of the standards are as follows:

Kapton: H 2.64%, C 69.13%, N 7.33%, and O 20.90%;
and Mylar: H 4.20%, C 62.50%, and O 33.30%. After some manipulations equation (1) reduces to

$$(C_A)\ \text{coal} = \frac{(H_A,o/Q)\ \text{coal}}{(H_A,o/Q)\ \text{standard}}\,.\,\frac{\left(\frac{dE}{dx}\Big|_{Eo}\right)\ \text{Coal}}{\left(\frac{dE}{dx}\Big|_{Eo}\right)\ \text{standard}}\,.\,(C_A)\ \text{standard} \qquad (2)$$

Equation (2) was utilized in evaluating the concentrations of H, C, N and O in coal samples.

3. Results and Discussion

PIXE results for minor and trace elements in Nigerian Enugu coals are presented in Table 1. It is essentially the concentration of the ash-forming inorganic constituents. The concentrations of minor and trace elements are quite important in the conversion techniques and quality upgrading processes of coal. Each data represents the average of three independent determinations. The results are fairly consistent for all the twenty four samples and show an accuracy of 7-10% of concentration for most of the significant elements. Fig.1 shows a typical x-ray spectrum for coal samples. Comparisons of present data are made with those of Borishade et al [5] and Hannan et al [4] who made use of INAA technique for the determination of concentrations of most of the elements.

Referring to Table 1, for aluminium, the average of present measurement is lower than that of Borishade et al. However, it is not surprising that the value presented by Hannan et al is a little higher than the present measurement, since Hannan's data is the average of all Nigerian sub-bituminous coals, which includes Enugu coal. For the determination of the concentration of silicon, Borishade et al used FNAA technique, which was based on the nuclear reaction $^{29}Si(n,p)^{29}Al$ as a result of exposure of coal samples to 14 MeV neutrons. Their value of 1.50 is significantly higher than the present measurement of 0.55.

The concentrations of sulphur range between (0.82-0.99)%, with an average of 0.87%. This is reasonably low and acceptable for most utilization. High standards of efficiency of coal burning furnaces are required with minimum environmental pollutants. Consequently, due to the low sulphur content, Nigerian Enugu coals would be ideal feedstocks for gasification plants. The sulphur contents of Nigerian coals generally range between 0.52 and 2.04% [5]. Borishade et al average data of 0.58% for sulphur using ASTM technique is in reasonable agreement with the present data. Similarly, their average data of 0.76 for sulphur obtained using ASTM technique on all Nigerian sub-bituminous coals is also in good agreement with the present measurement.

In the case of Iron, the present measurement of 0.079 is in good agreement with Borishade et al data of 0.06. However, Hannan et al's data of 0.28, which is the average of all Nigerian sub-bituminous coals is significantly higher. It is worthy of note that in the case of calcium, the present measurement of 201ppm is in very good agreement with Borishade et al's data of 200ppm. The present data are also in good agreement with Hannan's data for V, Cr and Br. However, there are significant differences for Mn and Sr.

The chemical analysis of ash is presented in Table 2. The present results for Fe_2O_3, TiO_2 and CaO show very good agreement with N.C.C. data. However, data for SO_2 and Al_2O_3 show appreciable difference, and significant difference in the case of K_2O.

The concentrations of C, O, H and N in Nigerian Enugu coal samples using HEBS technique are presented in Table 3. Each value represents the average of four measurements. The accuracy of data are generally less than ± 8%. Results for C, O and H are very consistent, however, the range of data for Nitrogen is fairly wide. Comparison of data with those of Borishade et al using ASTM technique and Nigerian Coal Corporation (N.C.C.)[1] are made in Table 4. In the ASTM method, Borishade et al determined the concentration of oxygen by subtracting the sum of other major components from 100%. The agreement of the present measurement with the previous data is generally good.

The elements which contribute to calorific value include C, H, N and S, while the moisture measurement is determined by the total hydrogen and oxygen contents. The ratio of carbon-to-oxygen (C:O) of 5.71 in the present measurement falls within the range of sub-bituminous coals in Nigeria according to the classification suggested by [10] and [11]. Thus Enugu coals are sub-bituminous, and represent most coals in Nigeria. Hannan et al and Borishade et al had shown that the majority of Nigerian coals are sub-bituminous. Also, in agreement with Borishade et al's finding, the present range of (4.49-5.16)% and an average value of 4.85% for hydrogen is high and conform with the generally high hydrogen values of Nigerian coals.

4. Conclusion

PIXE and HEBS techniques were employed for the measurement of concentrations of the major, minor and trace elements in the main Nigerian Enugu coals. The two techniques provide the indirect determination of the ash content and calorific values. The PIXE results are reported and compared with an earlier work on Nigerian coal using FNAA and INAA analytical methods while HEBS results are compared with ASTM previous data. The agreement between the present results and previous data is generally good. The results further support the claim that Nigerian coals are of weak and noncoking grades with low sulphur (0.82-0.99)% and relatively high hydrogen (4.49-5.16)%. The low percentage of sulphur in Enugu coals makes it acceptable for most utilization.

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TABLE CAPTIONS

Table 1 Elemental compositions of minor and trace elements in Nigerian (Enugu) coals.

(a) Borishade et al [5] using INAA technique on Enugu coals.

* FNAA technique on Nigerian sub-bituminous coals. (Enugu coal is sub-bituminous).

† ASTM technique on Enugu coals.

†† ASTM technique on Nigerian sub-bituminous coals.

(b) Hannan et al [4]. Results are the average concentration for Nigerian sub-bituminous coals using INAA technique.

* FNAA technique on Nigerian sub-bituminous coals.

Table 2 Comparison of chemical analysis of ash results with previous N.C.C. data.

Table 3 The main elemental compositions of Nigerian Enugu coals using HEBS technique.

Table 4 Comparison of major elemental compositions with previous data.

† ASTM technique on Nigerian sub-bituminous coals.

Table 1

AVERAGE OF RUNS ON THREE SAMPLES	Al (%)	Si (%)	S (%)	Fe (%)	P (ppm)	Cl (ppm)	K (ppm)	Ca (ppm)	Ti (ppm)
1	0.64	0.53	0.86	0.078	358	161	43	234	358
2	0.53	0.55	0.85	0.083	360	136	51	250	353
3	0.55	0.53	0.83	0.079	358	141	35	223	336
4	0.49	0.53	0.84	0.080	389	164	30	222	353
5	0.51	0.57	0.86	0.079	383	155	25	176	357
6	0.51	0.55	0.86	0.076	384	114	16	149	353
7	0.61	0.53	0.85	0.072	341	110	17	152	374
8	1.14	0.57	0.97	0.082	271	120	46	202	416
Range	0.44-1.28	0.53-0.57	0.82-0.99	0.072-0.082	271-431	101-242	16.0-68.3	146-264	328-423
OVER-ALL AVERAGE	0.62	0.55	0.87	0.079	356	138	33	201	363
(a)	0.95	1.50*	0.58^{+},0.76^{++}	0.06		41	64	200	855
(b)	0.77	1.50*		0.28		73	272	392	915

Table 1 cont.

AVERAGE OF RUNS ON THREE SAMPLES	V (ppm)	Cr (ppm)	Mn (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Ga (ppm)	GR (ppm)	Se (ppm)	Br (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Pb (ppm)
1	12.5	6.9	13.8	4.7	4.5	5.6	5.3	4.9	5.0	1.0	4.0	2.5	9.7	5.8
2	-	6.1	13.9	4.1	5.3	8.1	5.2	4.4	5.3	1.2	4.0	2.8	8.9	3.4
3	-	7.4	11.3	3.3	4.4	4.8	5.4	4.1	4.3	-	3.9	2.5	8.8	4.5
4	9.7	-	11.4	4.5	3.5	4.2	5.3	4.0	4.9	0.9	4.1	3.2	10.7	3.9
5	8.7	-	7.5	4.0	3.4	3.1	5.4	3.8	4.8	1.0	3.6	2.5	11.0	-
6	-	6.9	7.5	3.8	4.0	2.0	5.6	4.4	4.8	1.5	3.6	2.6	12.9	-
7	-	7.0	8.0	3.6	2.2	2.0	5.4	3.8	4.0	1.0	2.2	2.7	11.8	3.4
8	-	-	-	10.9	10.8	-	12.5	-	-	-	-	-	15.6	-
OVER-ALL AVERAGE	10.3	6.9	10.5	4.9	4.8	4.3	6.3	4.2	4.7	1.1	3.6	2.7	11.2	4.2
(b)	12.1	8.8	99.3							0.9	23			

Table 2

	SO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	CaO (%)	K_2O (%)
THIS WORK	55.82	37.57	3.63	1.96	0.90	0.13
N.C.C.	65.4	26.6	3.4	2.0	0.9	0.5

Table 3

	COAL 1		COAL 2		COAL 3		COAL 4		RANGE	AVERAGE
	KAPTON	MYLAR	KAPTON	MYLAR	KAPTON	MYLAR	KAPTON	MYLAR		
CARBON(%)	69.10	67.09	69.21	67.18	69.41	67.89	69.45	67.43	63.62-77.45	68.35
OXYGEN(%)	12.18	12.32	11.71	11.83	11.35	11.49	12.41	12.55	11.32-12.56	11.98
HYDROGEN(%)		4.72		4.86		4.96		4.86	4.49- 5.16	4.85
NITROGEN(%)	1.94		2.62		2.84		1.65		1.65-2.84	2.26

Table 4

	C (%)	O (%)	H (%)	N (%)
THIS WORK (HEBS)	68.35	11.98	4.85	2.26
BORISHADE et al (ASTM)	68.53	9.16	5.56	1.92
	73.00+	10.52+	5.81+	1.90+
N.C.C.	61.5-69.4	8.1-13.5	4.3-5.2	1.2-2.0

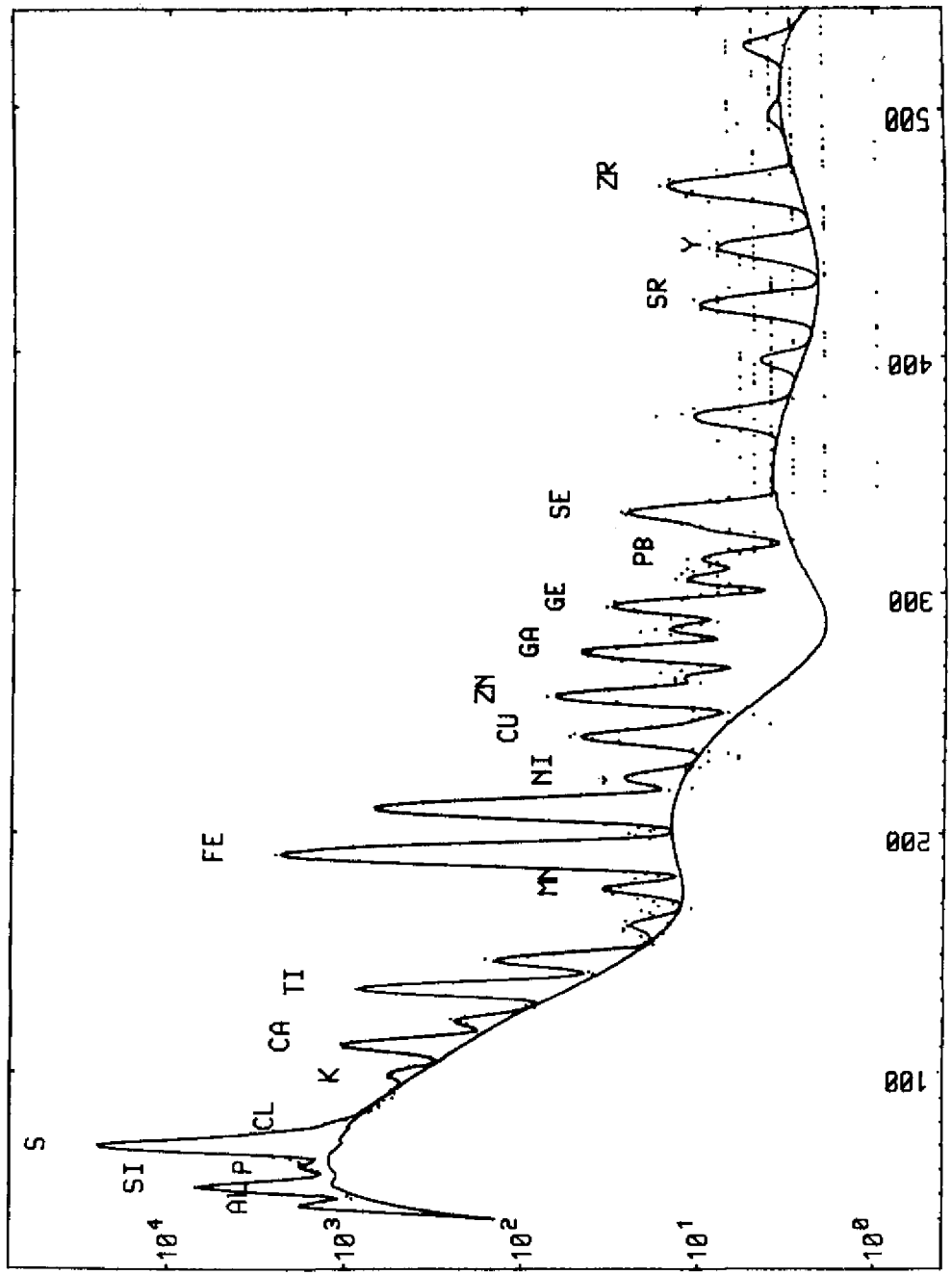

Fig.1 A typical X-ray spectrum of Nigerian Enugu coal samples.