Leaching of Trace Elements in Enugu Coal: Effect of Acid Concentration

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Abstract— *The effect of acid concentration on the trace elements composition of Enugu sub-bituminous coal from Onyeama Mine was investigated by leaching the coal using nitric acid (HNO_3) of 0.5M, 1.0M, 1.5M and 2.0M concentrations. The amount of trace elements (in ppm) present in the filtrate from the leaching process were determined using Varian AA240 Atomic Absorption Spectrophotometer with cathode lamps of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), and lead (Pb). Optimum leaching condition of the trace metals were obtained using 2.0M HNO_3 solution for 1 hour and 75µm particle size which resulted in the detection of As(1.363ppm), Cu (1.413ppm), Cr (0.764ppm), Cd (0.146), and Pb (1.942ppm). 2.0M concentration of nitric acid has proven to be very effective in the leaching of trace metals in Enugu coal. Result of the SEM analysis shows that the porosity of the coal residue was increased and this provides strong evidence that significant amounts of inorganic elements were removed. Onyeama coal, therefore, contains large proportions of silica, calcium carbonate, and dolomite, as well as some elements such as aluminum, iron, and potassium, and other trace metals such as lead, chromium, cadmium, arsenic, mercury, copper.*

Keyword— Atomic Absorption Spectrophotometer, Coal, Leaching, Trace elements.

I. INTRODUCTION

Coal, a naturally occurring combustible solid, is one of the world's most important and abundant energy sources. From its introduction 4,000 years ago as a fuel for heating and cooking to its nineteenth, twentieth and twenty first-century use in generating electricity, and as a chemical feedstock, coal along with oil and natural gas , has remained an important source of energy.

In Nigeria today, there is renewed interest in coal deposits by the federal government. This is aimed at diversifying the economy that has been solely dependent on crude oil and its refined products. Nigeria has one of the largest coal deposits in Africa. Nigeria's coal reserves are large, over 2 billion metric tons of which 650 million tons are proven. If fully revitalized, the coal industry could fetch up to a billion naira in export earnings [1].

Combustion of coal is a potential source of several trace element emissions to the atmosphere including heavy metals. Coal is the most abundant fossil fuel used throughout the world for production of electricity. Coal-fired power plants release to the environment SO_2 and NO_x as well as CO_2 and N_2O_5. Arsenic, cadmium, lead, and mercury are highly toxic to most biological systems at concentration at critical levels. Different trace elements in coal have different distribution characters in coal combustion. Inorganic matrices were shown to alter the concentration and occurrence of semi-volatile trace elements (As, Sb, Se) in the gas phase and these observation were attributed to specific interaction of ionic trace element species with cationic matrices [2]. The distribution and concentration of trace elements in coal are important from the environmental point of view, since they predict the behavior of these elements as they are released into the atmosphere when the coal is burned [3]. With increasing use of coal, the growing impact on the environment from the Potentially Hazardous Trace Elements (PHTEs) becomes a great concern [4]. The presence of trace elements like copper (Cu) and nickel (Ni) that causes corrosion of turbines and also poison catalyst, lead (Pb) and cadmium (Cd) which is toxic to humans, in coals, necessitate incorporation of a procedure for removing these metals before combusting or refining coal.

Atomic Absorption Spectrophotometer has been presented for determining the concentration of trace elements in coal, while the process of leaching with an acid has proven to be a successful method of removing trace elements in Enugu sub-bituminous coal.

II. MATERIALS AND MEHODS

2.1 Materials

Enugu sub-bituminous coal was gotten from Onyeama Mine in Enugu State, Nigeria. All reagents used were of Analar grade and are products of BDH Chemicals Ltd. Poole, England. Varian AA240 Atomic Absorption Spectrophotometer was used for the AAS analysis.

2.2 Methods

2.2.1 Sample preparation

The coal sample obtained from Onyeama mine was crushed and ground with mortar and pestle and screened through 20, 40, 63 and 75µm sieves mounted on a shaker. The coal sample was kept in an oven at 60^0C for one hour to dry and subsequently cooled in a dessicator.

2.2.2 Proximate Analysis

The prepared coal sample of definite size (75µm) was characterized to determine its moisture content, ash content, volatile matter, bulk density and fixed carbon using ASTM methods.

2.2.3 Digestion of Virgin Coal

2grams of oven-dried coal sample was measured into a $250cm^3$ round – bottomed flask and $50cm^3$ mixture of hot concentrated nitric (800ml/L) and perchloric (200ml/L) acids was added. The flask was then connected to a 50cm tall vigorous column, which was connected to a 25cm condenser unit. The entire assembly was mounted on an electric heating plate. The sample was digested for 8hours until clear solution was obtained. The solution was cooled and filtered through acid – washed filter paper and then adjusted to a volume of $100cm^3$ using distilled water.

A blank reagent (without sample) was prepared using a $50cm^3$ mixture of nitric acid and perchloric acids in a $250cm^3$ round-bottom flask, and the entire sequence of steps was followed as described for the sample preparation. The sample solution and the blank solution were analyzed for lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As) and copper (Cu).

2.2.4 Leaching of the coal sample

2g of the pulverized coal sample was measured into a 50ml beaker containing 0.5M of nitric acid. The mixture was shaken vigorously and then placed in a water bath set at 60^0C for 1 hour with intermittent stirring. After 1 hour, the mixture was filtered using a Whatman filter paper No. 1, into reagent bottles and the filtrate was taken for trace metal analysis using Atomic Absorption Spectrophotometer with hollow cathode lamps of copper, chromium, cadmium, arsenic and lead. The entire procedure was repeated several times to study the effects of different nitric acid concentrations, particle sizes and contact time on the leaching of the trace metals. The mean of the results were taken and their standard deviation recorded.

2.2.5 AAS Analysis

Varian AA240 Atomic Absorption Spectrophotometer obtained at Springboard Research Laboratories, Awka, Anambra State, was used to analyze the filtrates from the leaching process.

2.2.6 SEM Analysis

To obtain the micrographs of the virgin and residual coal samples, Scanning Electron Microscope (SEM) analysis was carried out at the Department of Chemistry, Ahamadu Bello University Zaria Nigeria.

2.2.7 EDAX Analysis

Energy Dispersive X-ray (EDAX) analysis was carried out on both the treated and the virgin coal at Chemistry Department Ahmadu Bello University Zaria Nigeria to analyze the elemental constituents of the coal samples.

III. RESULTS AND DISCUSSION

3.1 Proximate Analysis

The result of the proximate analysis of the coal is presented in table 1.

Table.1: Proximate analysis of the coal sample used

Parameter	Amount (%)
Moisture content	8.4
Ash content	10.2
Volatile matter	24.6
Sulphur	1.1
Fixed carbon	42.8

3.2 Effect of acid concentrations on the leaching of trace metals at 1hr and 75µm

Table.2: Amount of trace metals (ppm) detected at constant 1hr and 75µm.

Acid Concentration (mol/dm^3)	As	Cu	Cr	Cd	Pb
0.5	0.301	0.640	0.582	0.134	1.486
1.0	0.650	1.202	0.210	0.045	0.980
1.5	1.212	1.222	0.000	0.003	0.704
2.0	1.363	1.413	0.764	0.146	1.942
Mean	0.882	1.119	0.389	0.082	1.278
Standard Deviation	1.322	1.679	0.584	0.213	1.917

3.3 Effect of contact time on the leaching of trace metals at 2.0M HNO_3 and 75µm

Table.3: Amount of trace metals (ppm) detected at constant 2.0M HNO_3 and 75µm.

Contact Time (hours)	As	Cu	Cr	Cd	Pb
1	1.322	1.321	0.616	0.057	1.605
2	1.411	1.430	1.047	0.062	1.955
3	0.805	0.952	0.000	0.003	0.283
4	0.714	0.423	0.000	0.001	0.002
Mean	1.063	1.032	0.416	0.031	0.961
Standard Deviation	1.595	1.547	0.624	0.046	1.442

3.4 Effect of particle sizes on the leaching of trace metals at 1hr and 2.0M

Table.4: Amount of trace metals (ppm) detected at constant 1hr and 2.0M.

Particle sizes (µm)	As	Cu	Cr	Cd	Pb
75	1.104	1.001	0.594	0.123	1.124
63	0.922	0.540	0.470	0.039	1.019
40	0.000	0.333	0.396	0.026	0.728
20	0.000	0.052	0.000	0.003	0.441
Mean	0.507	0.482	0.365	0.048	0.828
Standard Deviation	0.759	0.722	0.547	0.072	1.242

The coal leaching process has five trace element of interest namely; Arsenic (As), copper (Cu), chromium (Cr), cadmium (Cd), and lead (Pb). The results obtained for different acid concentrations, contact times and particle sizes are presented in tables 2, 3, and 4, respectively. Copper, cadmium and lead were detected in all the samples analyzed.

In table 2, optimum leaching condition of the trace metals was obtained using 2.0M HNO_3 solution for 1 hour and 75µm particle size which resulted in the detection of As(1.363ppm), Cu (1.413ppm), Cr (0.764ppm), Cd (0.146), and Pb (1.942ppm). The amount of trace metals detected in table 3 increased as the leaching time increased from 1 hour to 2 hours, after which a drop was noticed. There was an increase in the amount of trace metals detected as the particle sizes decreased in table 4. This is as a result of an increase in the surface area available in the coal for leaching of the metals.

3.5 Scanning Electron Microscope (SEM) Observation

The SEM Micrograph of both virgin and leached coal sample are presented in figs. 1 and 2 below. The SEM micrograph of the coal samples were taken at a magnification of 10µm. It can be observed from the figure that a bulk of microstructure which in turn is composed of a homogeneously distributed network comprised of small filamentous and fistulous crystallites showing the presence of minerals. The bright luminosity indicates the presence of lithophytes like magnesium, aluminum, silicon, calcium, titanium etc, and sidrophytes, like iron, and the dark luminosity indicates the presence of chalcophiles like lead, chromium, cadmium, arsenic, copper, etc. Etched pits, layers, some islands and hills and valleys can be seen randomly distributed throughout the micrograph. These might have resulted from dolomite like $CaMg(CO_3)_2$ and calcites like $CaCO_3$, or their assemblage due to the thermal shock during metamorphism.. Veins corresponding to iron oxides can also be seen. From the foregoing, Onyeama coal contains large proportions of silica, calcium carbonate, and dolomite, as well as some elements such as aluminum, iron, and potassium, and other trace metals such as lead, chromium, cadmium, arsenic, mercury, copper. Numerous aggregated particles can also be seen in the micrographs. The porosity of the coal residue was increased and this provides strong evidence that significant amounts of inorganic elements were removed. However the surface coverage is still bright and luminous indicating the presence of mineral phases.

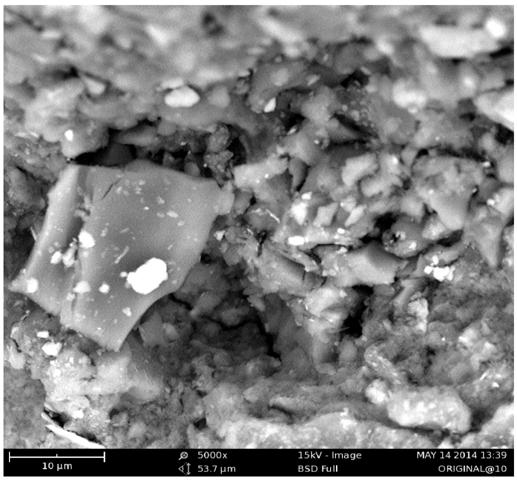

Fig.1: SEM Micrographs of virgin coal sample at 10µm

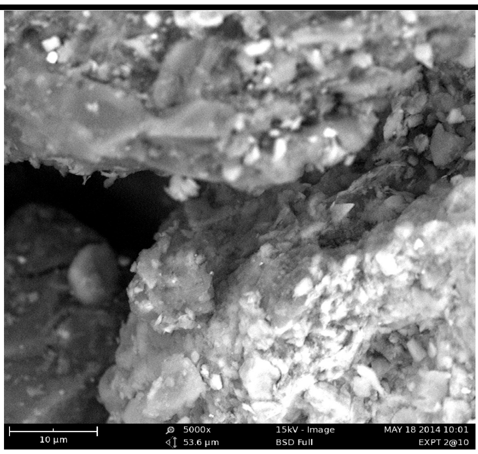

Fig. 2: SEM Micrographs of residual coal at 10µm

The SEM micrograph of the residual coals (fig. 2 above), revealed that the leachant employed caused morphological changes in the particles and did enormous harm to the surface by leaching some of the organic and inorganic elements.

3.6 EDAX Analysis

Energy Dispersive X-ray Spectrophotometric (EDAX) study of the virgin coal and residue coal samples were conducted to ascertain the elemental composition of the samples. The spectrums were taken at four different spot on the samples.

Table.5: Elemental analysis of Virgin Coal from EDAX spectrum.

Element	**Concentration (%)**			
	Spot 1	**Spot 2**	**Spot 3**	**Spot 4**
C	31.7	37.4	16.0	22.6
O	61.1	62.6	64.5	65.7
AL	4.0	-	-	-
Si	8.3	-	3.4	-
N	-	-	8.8	11.7
Br	-	-	7.3	-

It can also be seen that the virgin coal sample does not contain sulphur.

The elemental compositions were reduced after the leaching process as indicated in table 6 below.

Table. 6: Elemental analysis of the residue coal sample

Concentrations (%)				
Elements	**Spot 1**	**Spot 2**	**Spot 3**	**Spot 4**
C	22.1	24.8	18.2	2.4
O	58.1	54.8	71.6	64.7
Al	-	-	-	6.0
Si	4.6	10.9	10.2	18.5
N	9.4	-	-	7.0
Br	5.8	-	-	1.5

IV. CONCLUSION

The effect of different nitric acid concentrations, particle sizes, and contact time on the leaching of trace metals in Enugu coal was studied. It was found that these parameters have significant effect on the leaching of the trace metals in the coal sample. For the different acid concentrations, contact time and particle sizes studied, mean values of arsenic (0.882, 1.063and 0.507ppm), copper (1.119, 1.032 and 0.482ppm), chromium (0.389, 0.416 and 0.365ppm), cadmium (0.082, 0.031, and 0,048ppm), and lead (1.278, 0.961, and 0,828ppm) were recorded, respectively. Optimum leaching condition of the trace metals was obtained using 2.0M HNO_3 solution for 1 hour and 75µm particle size. 2.0M concentration of nitric acid has proven to be very effective in the leaching of trace metals in Enugu coal. SEM result also showed evidence of morphological changes in the residual coal sample.

REFERENCES

[1] S. O. Akande, H. Andreas and B.D. Erdtmann. “Upper Cretaceous and Tertiary Coals from Southern Nigeria: Composition, Rank, Depositional Environments and their Technological Properties”. Nig. Assoc. Pet. Explorationists Bull., 7, pp 26-, 1992.

[2] A. A. Raeva, O. V. Klykov, E. I. Kozliak, D. T. Pieerce, and W. S. Seames. “Insitu Evaluation of Inorganic Matrix Effects on the Partioning of three Trace Elements (As, Sb, Se) at the outset of Coal Combustion”. Energy Fuels, 25 (10), pp 4290-4298, 2011.

[3] L. D. Richard, D. F. S. Natusch, J. R. Wallace, and C. A. Evans. “Trace Elements in Fly Ash: Dependence of Concentration on Particle Size”. Environmental Science and Technology, 8 (13), pp 1107-1113, 1974.

[4] J. Zang, D. Ren, Y. Zhu, C.L. Chou, R. Zheng and B. Zheng. “Mineral Matter and potentially Hazardous Trace Elements in Coals from Qianxi Fault Depression Area in Southwestern Guizhou, China”. Int. J. Coal Geol., 57, pp 49-61, 2004.