



## Speciation of some selected heavy metals in coal bottom ash from Okaba Coal, Ankpa, Nigeria

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### ABSTRACT

Speciation of coal bottom ash from Okaba in Kogi State Nigeria was carried out using flame atomic absorption spectrometry. Results of this research showed that the elements studied (Cr, Fe, Cu, Ni, Pb, Cd and Zn) were all observed in at least three fractions of the sequential extraction procedure. Pb showed more presence in the exchangeable fraction ( $80 \pm 0.03 \mu\text{g/g}$ ) which is a serious problem to plants and human due to weathering activities in the soil. Most of the elements with high concentration in the residual fractions were found to be thermally stable and of low volatility (Cu and Zn). Chromium occurred mostly as a reducible fraction ( $80 \pm 0.02 \mu\text{g/g}$ ) while Fe occurred mostly as bound to carbonate species. Cadmium was generally low in all the fractions analysed. This trend may be attributed to high volatility of Cd species. Similarly, Ni had a distribution in all the fractions with the highest in the reducible fraction ( $39 \pm 0.01 \mu\text{g/g}$ ) and lowest in the carbonate bound fraction ( $24 \pm 0.01 \mu\text{g/g}$ ). The exchangeable fraction of the elements studied is consistent with previous studies of coal bottom ash speciation. The ash matrix may also have contributed to a significant rise in the concentration of Ni at the exchangeable fraction thereby leading to significant variations in metal concentration over the ash particle.

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### INTRODUCTION

Bottom fly ash is formed in coal furnaces. It is made from agglomerated ash particles that are too large to be carried in flue gases and fall through open grates to an ash hopper at the bottom of the furnace. Although trace metal contents are generally of little or no concern when considering ash utilization, they are of considerable importance in ash disposal practices due to possible environmental effects arising from leaching of

the ash. The availability of trace elements occurring in bottom ash depends on the physical and chemical forms of the elements. The basic chemical forms of metals contained in the environmental samples can be described by using sequential extraction procedure (Namiesnik, 2002; Sahuquillo et al., 1999; Tessier et al., 1979). Behaviours of trace elements in thermal treatments such as coal combustion have been reported by many

studies (Miller et al., 2002; Belén et al., 2003; Miller et al., 2006; Elled et al., 2007).

Bottom ash may contain significant amounts of some potentially toxic metals such as Cr, Cu, Ni, Fe, Pb, Cd and Zn. However, there are broad composition ranges for bottom ash which indicates the complex processes involved in the combustion and large variations between combustion sites and fuels. Previous research has shown how metals are partitioned during combustion. The partitioning of metals in different ash flows is the final results of a large number of physical and chemical processes occurring inside the combustion unit. Some metals such as Cd and Pb have been found to be mainly present inside fly ash particles, while Zn was discovered to be present both in the particle interior and on the surfaces (Camerani-Pinzani et al., 2004). Other metals such as Cd, Cu, Mo and Zn were found to be enriched on particle surfaces as acid soluble compounds, while Co, Mn, Ni and Pb were found both inside the particles and on the surfaces (Fujimori et al., 2002). Data are available that suggests that the ash matrix may have an influence on the distribution of volatile metals and may lead to significant variations in metal concentration over the ash particle (Camerani-Pinzani et al., 2002; Abanades et al., 2002). Metals such as Fe and Ca have been found to be associated with metals such as Cd, Cr, Pb and Zn in municipal solid waste ash particles, and Cd, Cu and Pb were found to be present in biomass ash particles rich in quartz (Lind et al., 1999; Camerani-Pinzani et al., 2007; Wan et al., 2006).

The aim of this work was to study the distribution of some selected trace metals in the feed coal bottom ash from Okaba coal mine.

## **MATERIALS AND METHODS**

### **Reagents**

All reagents used are analytical reagent grades. They include Ammonium acetate (NH<sub>4</sub>OAc), sodium acetate (NaOAc), glacial acetic acid (HOAc 100%), hydrogen peroxide

(H<sub>2</sub>O<sub>2</sub>), MgCl<sub>2</sub>, HClO<sub>4</sub>, HNO<sub>3</sub>, HF, NH<sub>2</sub>OH.HCl, distilled water.

### **Equipments**

The equipments used are IECCentra-CL centrifuge, test agitator, Hanna pH 211 Microprocessor pH meter, hot plate, timer, Mettler Toledo PR2002 electronic weighing balance, Buck Scientific atomic absorption spectrophotometer model AVG 210.

### **Sampling**

Coal fly ash was collected from Okaba town from consumers using coal as a source of energy for heating purposes. Predominantly, the inhabitants of the area use coal as a main source of energy for domestic use.

### **Method**

#### ***Sequential extraction procedure***

Sequential extraction procedure by the method of Tessier et al. (1979) was used to extract the metals from the ash into various fractions. A summary of the sequential extraction steps as used are shown in Table 1.

## **RESULTS**

The results of the distribution of some selected metals on coal bottom ash from Okaba are presented in Table 2 and Table 3. The analyses are carried six times and the mean and standard deviations calculated as indicated in the results Table. From the results, the observations of the various metals in from form of he exchangeable fraction in order of decreasing concentrations are Pb>Fe>Cr>Zn>Ni>Cu>Cd while that of bound to carbonate fraction appears as Fe>Cr>Zn>Ni>Cd>Cu>Pb. The Fe-Mn bound fraction were detected in the order Cr>Ni>Zn>Pb>Fe>Cd>Cu while the concentration at the organic bound fraction was observed in the order Zn>Ni>Cd>Cr>Fe>Cu>Pb. The observed concentration in the residual fraction occurred in the range Cu>Zn>Cr>Ni>Pb>Cd>Fe.

**Table 1:** Sequential extraction steps.

Steps	Extraction Condition	Target phase
1.	9 ml of MgCl <sub>2</sub> at pH 7, T=20 °C	Exchangeable (water soluble)
2	Residue + 8 ml distilled water, CH <sub>3</sub> COONa; CH <sub>3</sub> COOH. T=20 °C	Bound to carbonate (acid soluble)
3	20 cm <sup>3</sup> , 0.04 NH <sub>4</sub> OH.HCl in 25% CH <sub>3</sub> COOH T= 96 °C	Bound to (Fe-Mn) oxides (Reducible)
4	9 mL, 0.02M of HNO <sub>3</sub> , 5 mL of H <sub>2</sub> O <sub>2</sub> (30%), T=85% for 2 h, 3 mL H <sub>2</sub> O <sub>2</sub> , CH <sub>3</sub> COONH <sub>4</sub>	Bound to organic matter (oxidation)
5	Oven dried at 105 °C, 5 mL HNO <sub>3</sub> , 10 mL HF and 10mL HClO <sub>4</sub>	Residual fraction.

The extracts were stored in plastic containers for analysis using flame atomic absorption spectrophotometer.

**Table 2:** Results of speciation of heavy metals in bottom coal ash in µg/g.

Parameter	Number of ash samples	Exchangeable			Bound to carbonate			Bound to Fe-Mn oxide					
		Range µg/g		Mean	SD	Range µg/g		Mean	SD	Range µg/g		Mean	SD
		Min	Max			Min	Max			Min	Max		
Cr	6	49	51	50	0.01	58	60	59	0.01	72	88	80	0.02
Fe	6	66	68	67	0.01	70	78	74	0.04	05	09	07	0.01
Cu	6	08	12	10	0.01	08	1.2	01	0.01	0.9	1.1	01	0.01
Ni	6	29	47	38	0.21	21	27	24	0.01	38	40	39	0.01
Pb	6	77	83	80	0.03	ND	ND	ND		17	23	20	0.04
Cd	6	05	09	07	0.02	03	05	04	0.01	3.8	4.2	04	0.01
Zn	6	39	59	49	0.32	35	37	36	0.01	38	40	39	0.01

**Table 3:** Results of speciation of heavy metals in bottom coal ash in µg/g – continued.

Parameter	Number of ash samples	Bound to organic matter			Residual fraction				
		Range µg/g		mean	SD	Range µg/g		Mean	SD
		min	max			Min	Max		
Cr	6	03	05	04	0.01	63	69	66	0.01
Fe	6	ND	ND	ND		ND	ND	ND	
Cu	6	ND	ND	ND		72	74	73	0.01
Ni	6	31	41	36	0.04	22	38	30	0.03
Pb	6	ND	ND	ND		27	33	30	0.02
Cd	6	04	14	09	0.07	06	08	07	0.01
Zn	6	60	72	66	0.05	67	71	69	0.02

N = number of ash sample; ND = not detected

## **DISCUSSION**

To better understand the distribution of trace metals during the roasting of coal, Tessier et al. (1979) method was adopted. From the results, sequential extraction indicated that Cr mainly occurred as bound to Fe-Mn oxide ( $80 \pm 0.02 \mu\text{g/g}$ ) in the bottom ash. This is an indication that a significant amount of Cr would have been retained in sulphides as well (Abanades et al., 2002). The amount of Cr in the residual fraction ( $66 \pm 0.01 \mu\text{g/g}$ ) is also an indication that crystalline minerals/silicates were the main hosts for Cr. The high values of Cr observed in all the fractions are an indication of the non-volatility of Cr during roasting and is consistent with predictions from the thermodynamic model (Diaz et al., 2006).

Iron occurred mostly as carbonates as indicated in the result with a value of  $74 \pm 0.04 \mu\text{g/g}$ . The exchangeable fraction of Fe was observed as  $67 \pm 0.01 \mu\text{g/g}$ . This is also an indication that sulphates of Fe are present in the bottom ash. The low concentration of Fe in the oxidizable fraction ( $07 \pm 0.01 \mu\text{g/g}$ ) may plausibly signify that less Fe is bound to sulphides and organic matter. This assertion may be observed in the non-detectability of Fe in the organic matter.

Copper in this speciation study occur mostly as a residual fraction with concentration of  $73 \pm 0.01 \mu\text{g/g}$ . This may be attributable to the high chemical stability of Cu in the acidic washing water. Nickel has concentrations  $< 40 \mu\text{g/g}$  in the bottom ash fractions and are mainly associated with oxides. These low concentrations at various fractions may be a reflection of their weak volatilities during oxidation of Ni-bearing sulphides. This observation is consistent with the thermodynamic modelling result that Ni would not vapourize from raw materials at  $85^\circ\text{C}$  (Frandsen et al; 1994). Organically associated Ni was also observed as  $36 \pm 0.04 \mu\text{g/g}$ . The concentration of Ni in the residual fraction ( $30 \pm 0.03 \mu\text{g/g}$ ) may suggest that most of sulphide – associated Ni were incorporated with silicates or crystalline Fe-oxides during the combustion. Previous

studies also suggested that Ni could be easily incorporated into iron oxides via the formation of strong bonds during thermal treatments

Lead occurred mainly as exchangeable fraction in the speciation studies ( $80 \pm 0.03 \mu\text{g/g}$ ), the reducible fraction is  $20 \pm 0.04 \mu\text{g/g}$  while the residual fraction is  $30 \pm 0.02 \mu\text{g/g}$ . The high value of Pb in the exchangeable fraction indicates that, although it is not the primary mechanism for Pb to sink out of the ash, simple physical adsorption/Condensation on fine particles also occurs. The high concentrations of sulphur compounds in the ash may have significantly enhanced the physical adsorption of gaseous Pb as condensed sulphate on the surface of bottom ashes (Diaz et al., 2006). The observed trend of residual Pb may probably be related to the formation of thermostable compounds through chemical between gaseous Pb species and silicates. The Fe-Mn oxide bound fraction of Pb implies that the chemical adsorption to Fe – Mn oxide could also play a role in the deposition of gaseous Pb. These could also be ascribed to the high thermostability of amorphous Fe – Mn oxides. Cadmium primarily was detected at low concentrations in all the fractions considered. The low concentrations of Cd observed is consistent with the thermodynamic prediction that Cd tends to vapourize as Cd(g) and CdO(g) at the furnace temperature. Significant enrichment of Cd in bottom ashes has been observed in previous fuel and coal combustion studies (Häsänen et al., 1997 and Yan et al., 1999). Elements partially or fully vapourized during roasting usually undergo further transformations and partitioning downstream as the flue gas cools, including condensation, physical adsorption, chemisorptions or chemical reactions Ratafia–Brown 1994 and Xu et al., 2003).

Zinc was observed in the bottom coal ash primarily as residue ( $69 \pm 0.02 \mu\text{g/g}$ ). This distribution also indicates that the residual, organic bound and exchangeable species are the main forms of Zn in the bottom ash. Previous work has shown that Zn sulphides

can be readily weathered to form hydrated Zn sulphates, carbonates or other acid exchangeable species (Cui et al., 2002). As part of the reasons why exchangeable and Fe-Mn oxide Zn have moderately low concentrations, acid exchangeable Zn species in coals tend to volatilize with limited vapourization, and subsequently interact with other ash species during combustion at 1500 °C. The elevation of residual Zn in the combustion wastes was probably caused by the reactions between Zn (in particular, sulphide Zn) and iron oxides and/or silicates during combustion. Previous studies have reported the formation of stable ZnO.Fe<sub>2</sub>O<sub>3</sub>(s) through interactions between Zn and iron oxides (Folgueras et al., 2003). Then high concentration of iron oxides in the combustion system could have facilitated Zn and iron oxide interactions.

### Conclusion

The distributions of potentially harmful heavy metals in bottom ash showed that Pb occurred substantially in the exchangeable phase. Fe occurred mostly as carbonate bound and exchangeable species. Chromium occurred mostly in the reducible and residual fractions. The observed fraction of Cu occurred at the residual phase. Nickel was almost evenly distributed in all the steps used in the sequential procedure. Cadmium was not detected in large quantities in all the steps plausibly due to its high nature of volatility. Zinc occurred mainly in the residual and organic bound fraction. However, the exchangeable fraction of Zn equally exhibited elevated concentrations. The above conclusions as drawn from this research may be attributable to the occurrence of trace elements in coal ores and the thermostability of formed trace metal species in the transformations of the selected trace elements during combustion. Elements that were present in acid exchangeable species (Fe, Ni, Pb) were readily liberated during combustion. Low thermostability elements (Cr, Cu Zn) were primarily vapourized; while those elements that tend to form species with high

thermostabilities (Fe, Ni, Pb, Cd) mainly reacted with other materials which remained in the solid residues.

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