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Calcium and Heavy Metal Concentrations in Coal and Combusted Coal Ash, as Well as their Toxicity, Measured Using Atomic Absorption Spectrometer.

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ABSTRACT

Calcium is an essential mineral for all living organism, so also are some heavy metals but there are some heavy metals that are not useful to living organism, like lead (Pb) which are very toxic. In this study, the concentration of calcium and heavy metals in coal and bottom coal ash was evaluated with the use of Atomic absorption spectrometer (AAS), the result obtained shows that the concentration of calcium (Ca) in bottom coal ash which is 1380.50 mg/kg, 0.1381%, is far higher than the concentration of calcium in coal which is 25.55 mg/kg, 0.0026%. This may be due to the thermal process coal undergoes in the coal fired burner plant before steams are transferred to the turbine. We also noticed that calcium interacts with other heavy metals. The concentration of heavy metal shows that lead (Pb) has the highest concentration in both bottom coal ash and coal, lead which is a toxic substance even at low concentration

KEY WORDS: Heavy metals; calcium; toxicity; coal and bottom coal ash

INTRODUCTION

Calcium bearing minerals are one of the main typical minerals in coal and coal ash, in the process of coal thermal conversion , calcium bearing minerals undergoes different morphological and physiological transformation in which the reaction such as temperature, pressure are important factors . [1] This calcium bearing minerals also play an important role in influencing coal combustion and gasification processes. Looking at the chemical composition and properties of coal, coal with CaO content with more than 15% is identified as high calcium coal. [2] After combustion minerals and other organic component in coal breaks down forming ash and slag. [3] Calcium carbonate is a chemical compound with the chemical formula $caco_3$, it is a common substance found in rocks as the mineral calcite and aragonite , it has a medical use as calcium supplement or as an antacid, but excessive consumption of calcium is hazardous to human and plant, it causes hypercalcemia and digestion issues [4]. Calcium is an essential plant nutrient responsible for integrity of cell and plant structure, yet it is generally neglected because it is available in plant in must cultivated soil, only in an acidic soil requires addition of calcium fertilizer, also in liming soil it is applied as gypsum. [5] Calcium is necessary in human in many perspectives including the formation of strong bone and teeth, blood control mechanism etc.

Coal is known to have originated from biological source , so is not a categorized as mineral, coal is believed to be generated from the remains of dead animals and plants deep beneath the earth surface where they are exposed to high temperature and pressure for extended period of time. Coal is a complex geological material composed mainly of organic matter and mineral. The mineral matter plays significant role in affecting the coal utilization process especially combustion. Minerals on its own are the major host of this element present in coal. [6] Coal is a none-renewable fossil fuel that is combust and used to generate electricity. Interestingly both mining technique and combustion are both hazardous to living organism. [7] Coal ash also known as combusted coal or combust coal residue (CCRs) is produced from the burning of coal in a coal fired powered plant. Coal ash includes a number of bye products from burning coal. This includes fly ash, bottom ash scrubber residue and fluidized bed combustion ash. For this study we will only be looking at the bottom coal ash. The comparison we are studying is between the heavy metal concentration and calcium concentration in coal and bottom coal ash

MATERIAL AND METHOD

STUDY AREA

Coal analyzed for this work was gotten from Zuma 828 coal mining site at Ankpa L.G.A of Kogi-state. Zuma 828 is a mining and exploration company which is into mining and it one of the licensed companies to mine coal from Okobo-Apiko. Okaba coal mine is a surface operating mine in Okaba,kogi-

state. It has a coordinate of (7024’28’’N, 7º48’6’’E) coordinate. Mindat.org. it production per ton is about 0.16 million ton per annum. [8]. While the bottom as coal ash was gotten from Obajana cement plant reject coal site. Obajana is situated in the north central area of Nigeria and it also in the north central area of kogi-state. It has a coordinate of (709104ºN, 64399ºE) the factory is located at the north central part of the state. [9] Obajana cement plant commissioned it’s coal mill to power it plant in 2014 due to the fact that it was cheaper to operate on. It coal source have been said to come from Enugu and other part of Nigeria including Okaba.

SAMPLE COLLECTION

Some quantity of coal was gotten from Zuma 828 coal mining site at Okaba-Okpiko , Ankpa Some sample of bottom coal ash was also collected from the coal reject at Obajana cement factory. All samples were sent to the lab. For analysis

SAMPLE ANALYSIS

1 gram of combusted coal was measured into a digestion flask, 200ml of 3:1 of HCl and HNO_3 was added to the same sample and heated in a digestion block for about 1-2 hours at 250ºc-350ºc, about 2-3ml of H_2O_2 was added to the mixture and it was subjected to heating for another 1hr for complete digestion. The digest obtained after heating was then transferred into a volumetric flask of 50mls and was marked up to the mark with deionized water. The digest sample was analyzed using atomic absorption spectrometer (AAS) for heavy metal analysis through the suction tube. Each of the trace mineral elements was read at their respective wavelengths with their respective hollow cathode lamps using appropriate fuel and oxidant combination. The meter reading for each element was used to calculate for the concentration of each element using the formula bellow. Same method was used to analyze the coal which was first grounded to powder before 1 gram was measured into the digest flask.

ppm or mg/kg (any of the elements) = Meter reading × Slope or Gradient × dilution factor.

%(any of the elements) =ppm or mg/kg divided by 10000 if result is needed in percentage when needed

Calculation

mg/kgSample = digest conc. x dilution factor

Digest conc. =Analytic reading on AAS

DF =$\frac{Vol.\ of\ digest \times aliquot}{weight\ of\ sample}$

Vol. of digest = Final volume of digested or extracted sample

Aliquot = ratio of sample to distilled water (when diluted further)

EXPERIMENTAL RESULT

TABLE 1:

EXPERIMENTAL VALUE GOTTEN FROM ANALYSIS OF BOTH COAL AND COMBUSTED COAL (BOTTOM COAL ASH)

S/N	Element	Concentration bottom coal-ash (mg/kg)	Concentration of coal (mg/kg)
1	Cadmium (Cd)	1.150	0.75
2	Lead (Pb)	160.85	178.65
3	Zinc (Zn)	20.75	13.35
4	Iron (Fe)	61.95	8.60
5	Manganese (Mn)	21.40	2.50
6	Nickel (Ni)	15.25	6.45
7	Chromium (Cr)	28.35	13.65
8	Copper (Cu)	7.65	1.70
9	Cobalt (Co)	10.20	2.45
10	Calcium (Ca)	1380.50	25.55
11	Magnesium (Mg)	94.90	89.10

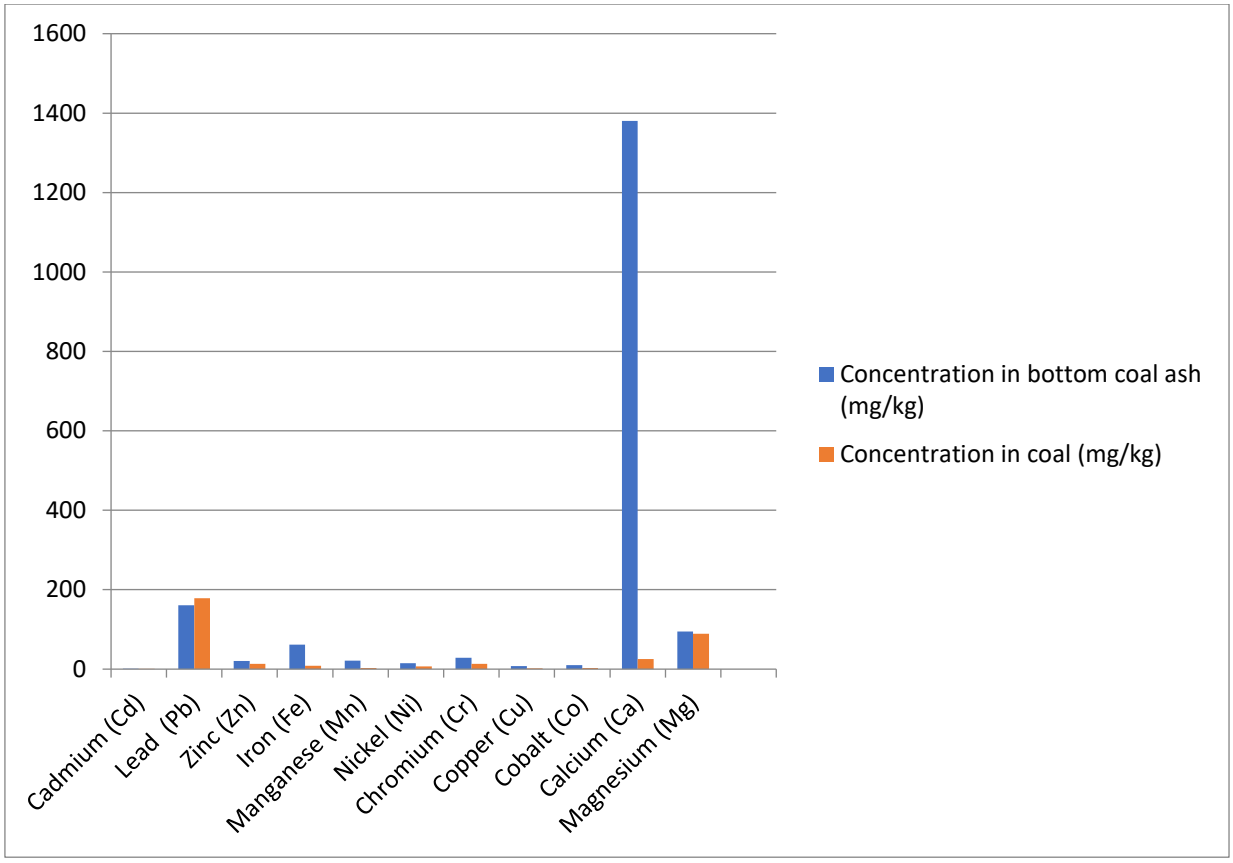

Figure 1: Chart showing the concentration of calcium and other heavy metals in coal and bottom coal ash

RESULT DISCUSSION

From the result obtained it was observed that the level of calcium in combusted coal (bottom coal ash) is far more than that in the raw coal from Zuma 828. We can actually by nature assume that is due to some chemical reactions or processes experienced during processing or thermal combustion (burning) of coal before steams are generated and transferred to the turbine. Considering the level of heavy metal in both coal and combusted coal you will notice that from our experimental work that in coal : Pb> Mg>Ca> Cr>Zn> Fe>Ni> Co>Mn> Cu> Cd in descending order. The concentration of lead in coal is 178.65mg/kg which in percentage is about 0.0179% and it the highest followed by magnesium which has a value of 89.10mg/kg (0.0089%) the next heavy metal in terms of concentration is calcium which has a value of 25.55mg/kg (0.0026%)followed by chromium 13.65mg/kg (0.0014%), zinc is the next 13.35mg/kg (0.0013%) followed by iron 8.60mg/kg(0.0009%) next is nickel which has a value of 6.45mg/kg(0.0003%) followed by cobalt 2.45mg/kg (0.0003%) followed manganese 2.50mg/kg(0.0003%) , the next is copper 1.70mg/kg(0.0002%) and the least element in terms of concentration is cadmium 0.75mg/kg (0.0001%) .

This was not the same for bottom coal ash. Calcium has the highest value of concentration of 1380.5mg/kg (0.1381%) followed by lead which has a value of 160.85mg/kg (0.0161%) the next element is magnesium which has a value of 94.90mg/kg(0.0095%) and it runs in the following descending order: Ca>Pb> Mg> Fe> Cr>Zn>Mn> Ni> Co> Cu> Cd. It was noticed that for combust coal some important trace element have high concentration but the presences of lead which is 160.85mg/kg has created a space for serious concern, this is because it concentration is far above the acceptable permissive value in the soil by WHO which is 100mg/kg. [10] In 11 august 2023 WHO made a statement on Exposure to lead which can affect multiple body systems and is particularly harmful to young children and women of child-bearing age. [11] There is no level of exposure to lead that is known to be without harmful effects. Young children are particularly vulnerable to lead poisoning because they absorb 4–5 times as much ingested lead as adults from a given source. But it fair enough to have calcium which is an essential element for all living organism with such a high level of concentration, this is not same for coal, lead which has a little or no biochemical importance has the highest value which gives reason for concerns, this is because it is a very toxic heavy metal and a pollutant to the environment. Adding phosphorous decreases availability of lead to plants. [12] It value is too far above the permissible concentration level for soil

Dietary calcium is well known to decrease gastrointestinal lead absorption and thereby reducing the risk of lead poisoning. [13]. High level calcium can result to hypocalcaemia, calcium is also important in bone formation with combination with other nutrient. [14] Interestingly calcium also interact with other heavy metal elements like zinc: calcium increases zinc excretion causing a decrease in the absorption rate of zinc in the body. [15] also high dietary calcium intake reduces zinc absorption, calcium also interacts with iron, and it inhibits iron absorption. [16] the application of calcium and sodium reduces chromium uptake in plants or crops. It application also help to reduce chromium toxicity. [17] Calcium helps in blood clotting, in muscle contraction and

in certain enzyme presentence in metabolic process. In cases where there are excessive potassium, sodium and magnesium, calcium is used as corrective elements. [18] But when magnesium and calcium are much it result to an undesirable formation of scale in drinking water. Calcium is an essential nutrient for plant, the level of calcium in plant should be 430-540ppm [19] (cropnuts). It is a major element in coal, it is in the form of calcium carbonate, calcium sulfate and there are also small amount of calcium chloride and calcium oxide. Calcium oxide and calcium carbonate has catalytic effect on the oxidation of organic matter in coal. ([20]-[21])

CONCLUSION

The concentration of heavy metals was determined in coal and combust coal and we have seen the concentration of calcium in both coal and combusted coal. We noticed that the level of concentration of lead in coal was far much more than that in combust coal and this was not the same for calcium whose level was high in combust coal, lead which has no biochemical importance was highest in coal which is of a great concern while calcium of great importance was present in combust coal , the toxicity of lead was discussed and we advise urgent measure should be taken to check mate this in both substance because it level is far above the permissible level in soil by WHO. Calcium in bottom coal ash is very high in concentration as compared to coal. Aside the high concentration of lead in both samples, the presence of other heavy metals could have been very interesting owing to the fact that their concentration in within the permissible threshold limit and they are of great biological importance to organism via a process of bioaccumulation. They are all needed by plants and animals for normal functions of the body system. We will therefore suggest that a means should be developed to reduce the concentration of lead in bottom coal ash, when this is done bottom coal ash will serve as a good source of soil nutrient, because the concentration of other minerals are very high in it even compared to its presence in coal and they are all within the permissible range of heavy metal in the soil. The emphasis of the work is lead discovered as a pollutant in the soil and should be checkmate to avoid it toxicity to living organism living in areas around it presence of coal site and dump site (reject coal site) and measured should be taken to incorporate other trace element in the soil as soil nutrition or mineral remedy. To the best of our understanding this is the first time this study is carried out.

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