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Full length research paper

Assessment of heavy metals and mineral compositions in some solid minerals deposit and water from a gold mining area of Northern Nigeria

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Mining of solid minerals has been identified as an entry point of heavy metals into the environment consequently polluting various components of the environment such as water and air. Five water samples and a kilogram each of selected solid minerals (Gold, tantalite and columbite) from one of the gold mines of Zamfara state were analyzed for mineral and heavy metals (Mn, Zn, Pb, Mg, Al, Cd, Cr, Ni, Co and Cu) using Atomic Absorption Spectrophotometer and Energy Dispersive X-Ray. The results revealed high concentration of Fe in columbite (2232.5±0.72) and tantalite (2202.5±0.92) higher than gold (108.1±2.64) while other elements were as follows; Mn (9.174±0.217), (1.56±0.43) and (0.56±0.83) in gold, columbite and tantalite respectively. Zn (2.67±0.104, 0.06±0.28 and 0.06±0.10) in gold, tantalite and columbite respectively while lead (87.02±1.029, 6.84±0.19 and 0.067±0.39) in gold, columbite and tantalite in that order. Tantalite was richer in bicarbonate mg/l (7.5), chloride mg/l (420) and sulphate mg/l (268.36) but lower in nitrate mg/l (750) than other solid minerals gold and columbite Heavy metals in water indicated significant contamination with water properties (Nitrate, calcium, conductivity and pH) and metals (Pb, 16.76±12.23; Cd 0.48±0.08) were higher than WHO standards. Water properties tested showed high temperature (19.10±0.01), pH was (5.30±0.15) and conductivity was (29.73±0.64). The study concluded that there was pollution of water body especially for toxic metals like Pb and Cd.

Keywords: Heavy metals, solid minerals, water and mining.

INTRODUCTION

Heavy metals occur naturally in rocks and soils but concentrations are frequently elevated as a result of pollution. Significant pollution of the environment due to heavy metals in the atmosphere has been reported by many authors, for example, pollution of fresh water occurs due to three major reasons which are excess nutrients from sewage, waste from industries, mining and agriculture (Sabhapandit et. al, 2010). Water pollution around the mining and smelting areas has been clearly demonstrated by high concentrations of heavy metals in water, sediments, and aquatic organisms (Nirmal et al, 2011).

.Contamination of soil and water occur in a number of ways simply classified as geochemical processes and human activities such as metal smelting industries, coal combustion and animal waste (Galadima et al, 2010). Besides the contamination from the weathering and leaching processes of mine tailings, untreated mine drainage also contributes large amounts of heavy metals to near by strems and rivers (Nirmal et al, 2011).

Mining of solid minerals has been identified as a major source of heavy metals in the environment because ore bodies generally include a range of minerals containing both heavy and essential metals. Opencast mines and underground mines are the most important and common methods of extraction of minerals from the earth (Sneha et al, 2012) suggesting the use of opencast mining especially in developing countries like Nigeria. A wide literature reported the presesnce of heavy metals in

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tillages of mining areas across the world (Popoola et al, 2011; Ezeaku, 2012; Concas et al, 2006). In most mining areas of Nigeria where illegal mining is commonly practiced, the interaction of solid minerals and the water sources is inevitable. In essence, water bodies such as rivers and lakes are used in floatation to separate the ore after crushing. The mining region of northern Nigeria is known since the colonial era. The popular among them is the Jos and in late 70's the Zamfara mining belt. The Zamfara mining region has deposits of precious metals like tantalite and gold among other (Alhassan et al, 2010).

In most developing countries like Nigeria, underground water has remained a major source of water to the teaming population of the people in the rural areas. Water quality assurance is therefore a collective responsibility. Water quality is to some extent an index of water pollution, the indices presently used in Nigeria are inadequate to indicate the damage that is done by heavy metals (Wakawa et al, 2008). The health implications of heavy metals like Ni, Pb, Co, Cr, Al, Zn and Cd had been fully documented. Significant contamination of seeds, plants and plant products with toxic chemical elements due to contaminated soil and water has been observed as result of release of these toxicants into the sea, rivers and even into irrigation channels. Afterwards, the consumption of contaminated vegetables constitutes an important route of animal and human exposure (Sajjad *et al,* 2009).

Heavy metals become toxic to the body when they are not metabolized by the human body thereby accumulating in the soft tissue, some of these metals such as Cd and Pb, injure the kidneys and cause symptoms of chronic toxicity (Okunola et al 2011).

This study determined the heavy metals Mn, Zn, Pb, Mg, Al, Cd, Cr, Ni, Co and Cu enrichment of selected solid minerals (Gold, Columbite and Tantalite) in the mining areas of northern Nigeria where lead poisoning occurred with death of about eighty children within one hundred and twenty days in this study site occurred. The heavy metals in the water in the area were also determined. The results were compared among the solid minerals and the water with a view to establish the relationship if any between solid minerals as major source of heavy metals in the mining area and as a pollution source to water bodies and to the environment as a whole.

MATERIALS AND METHODS

All glass wares used in the analysis were initially wash with liquid soaps, rinsed with distilled water and soaked in 10% HNO3 overnight; cleaned with distilled water according to Babale et al (2011).

Study Area

Yargalma is a small community of not more than three thousand people. It is located about 6 KM off Gummi- Bukkuyum road in Bukkuyum local Government area of Zamfara state in Northern Nigeria. The major occupation of the rural dwellers is farming activity until in the early eighties when tantalite and columbite were discovered in the area and the exploration reduced in early nineties due to low patronage, poor exploration technology and so on. The mining activity however, re-emerged within the last decade with the discovery of gold in the area. The state and the federal governments of Nigeria estimated that a total of over Four hundred children under the age of five died within four months and the statement was confirmed by the Medicin Sanfrontiers (Doctors without Borders). The main mining activity is not carried out in the community but artesian miners from the village bring the mined tillage into their houses to complete the isolation and purification. These processes include; milling and continues washing until the concentrate is gotten. Consequently, there is so much interaction with the tillage at homes including children, house wives and the aged ones.

Sample Collection and Treatment

Water samples were collected in ten plastic containers previously cleaned by washing in detergent, rinsed with tap water and later soaked in 10% HNO_3 for 24 hours and finally rinsed with deionised water prior to use. The samples were stored at 4^0C according to Akan et al (2009), while a kilogram each of solid minerals samples were packed into small plastic containers.

Digestion of Samples

The solid mineral samples were digested in which solid minerals samples were pulverized and air-dried in the oven at 30^0C to a constant weight and passed through a 2mm sieve. 1g of sample was placed in 100ml beaker. 15ml of 30% hydrogen peroxide was added. This was left to stand for 60mins until the vigorous reaction ceased. 15ml of concentrated HCl was added and the content heated gently at low heat on hot plate for about 2 hrs (Tsafe et al., 2012). The digest was then filtered into 50ml standard flask. Triplicate digest ion of each sample together with blank was also carried out. Then the analysis was conducted using flame Atomic Absorption Spectrophotometer (AA6500) at the National Research Institute for Chemical Technology, Zaria-Nigeria.

Table 1.0. The mean and standard deviations of Heavy metals concentrations (ug/g) of heavy metals in selected solid minerals (Gold, Tantalite and Columbite)

Metal	Metal Conc. in Gold (ug/g)	Metal Conc. in tantalite (ug/g)	Metal Conc. in columbite (ug/g)
Mn	9.175±0.217	0.56±0.83	1.56±0.43
Zn	2.67±0.104	0.06±0.10	0.06±0.28
Pb	87.02±1.029	0.067±0.39	6.84±0.19
Mg	9.25±0.215	ND	ND
Al	59.675±3.926	ND	ND
Cd	1.096±0.017	ND	ND
Cr	6.165±3.14	0.430±0.27	2.15±0.83
Ni	15.09±0.17	0.096±0.82	0.08±0.48
Co	16.88±0.83	0.144±0.62	0.06±0.51
Cu	1.28±0.065	0.067±0.29	0.14±0.01
Fe	108.1±2.64	2202.5±0.92	2232.5±0.72

*Footnote: Results are means of triplicate analysis while
*ND means; element not determined.

Water Digestion

50 ml of water samples were digested by addition of 10 ml of concentrated Nitric acid and 10 ml of hydrogen peroxide. This was heated on a hot plate to about half the original volume. The flask was allowed to cool, its contents was filtered into a 50ml standard volumetric flask and made up to the mark with distilled water according to Popoola et al (2011). The digest was then filtered into 50ml standard flask. Triplicate digest ion of each sample together with blank was also carried out. Then the analysis was conducted using flame Atomic Absorption Spectrophotometer (AA6500) at the National Research Institute for Chemical Technology, Zaria-Nigeria.

Sample Preparation for XRF Analysis

The pulverized samples of the solid minerals were passed through 355um sieve size and 0.3g was homogenized with 3mg of polystyrene dissolved in toluene serving as a binder. The pellets were formed by pressing at 10 tons with hydraulic press to form a pellet of about 19mm. the pellets were subjected for X-ray dispersive spectroscopy with specific emission properties reported by authors (Alhassan, et al, 2010; Hassan and Umar, 2004).

RESULTS

The results of the total heavy metals (Mn, Zn, Pb, Ni, Cu, Cr, Co, Mg, Mn, Al and Fe) concentrations (ug/g) in selected solid minerals (Gold, Tantalite and Columbite) in the mining area of Zamfara state of northern Nigeria were presented in table 1.0 below, showing the mean and standard deviations of a triplicate analysis of the samples. Table 2.0 present the percentage mineral compositions of the solid minerals in (Gold, Tantalite and Columbite) from an energy dispersive X- ray fluorescence showing the major and impurity oxides of metals. Table 3.0 present the anionic properties (mg/l) of the solid minerals (Gold, Tantalite and Columbite) showing the anionic enrichment of the solid minerals. Table 4.0 appraised heavy metals concentrations (mg/l) in water samples obtained from a hand dug well in the mining community showing the means and standard deviations of triplicate analysis and the results were compared with some national and International standards. Table 5.0 presents the water quality parameters of the water obtained from the site and the results were compared with some national and International standards.

DISCUSSION

The results of mineral oxides concentrations were highest in gold than th other solid minerals (tantalite and columbite) except for Fe in which columbite was highest (2232.5±0.72) and tantalite (2202.5±0.92). These were higher than Fe in gold (108.1±2.64). This concentration was not surprising because of the relative abundance of Fe in the earth crust and in solid minerals like tantalite and columbite, Fe is one of the major compositions of these solid minerals. Alhassan et al (2010), reported about the %Fe2O3 (7.87) in tantalite samples of Mai-kabanji indicating the presence of ilmenite in the sample. The result of this study did not followed a stable trend but showed some similarities between tantalite and columbite in metal contents with little deviation from each other but the two results of tantalite and columbite distinctively differed from Gold in their properties but typically associated minerals in Ta-Nb ore include zircon, rutile, monazite, cassiterite, ilmenite, garnet, uranium and gold (Adetunji et al, 2004). This further confirmed these metals (Ta and Nb) and their oxides have similar properties and behavior in their chemistry. Other mineral oxides were all highest in gold for example; Mn (9.174±0.217),

Table 2.0. Mineral properties of some Solid Minerals by XRF

Mineral oxide (%)	Gold	Tantalite	Columbite
CaO	0.245	1.039	3.442
TiO_2	1.5	6.00±0.07	1.753
V_2O_5	ND	1.145	0.965
Cr_2O_5	0.036	0.629	0.600
MnO	0.914	0.412	0.360
Fe_2O_3	3.295	3.220±0.19	5.896±0.20
NiO	0.991	0.112	0.140
CuO	0.071	0.084	0.079
ZnO	0.021	0.062	0.052
Ta_2O_5	ND	31.258±0.64	0.269
Ga_2O_3	ND	0.061	37.330±0.30
PbO	1.649	0.034	0.004
Rb_2O	ND	0.043	0.003
SrO_3	ND	0.008	ND
U_3O_8	ND	0.014	0.014
Nb_2O_5	ND	16.451±0.60	24.662±0.57
CoO	0.026	0.183±0.08	ND
CdO	0.024	ND	ND

Footnote: the values after ± are limits of detection while ND means element not determined.

Table 3.0. Anionic properties (mg/l) of the solid minerals presenting possible anionic Enrichment of the solid minerals

Parameter	Gold	Tantalite	Columbite
Nitrate (mg/l)	ND	750	1000
Bicarbonate (mg/l)	ND	7.5	5.0
Chloride (mg/l)	ND	420	180
Sulphate (mg/l)	ND	268.36	131.68

Footnote: ND means not determined

Table 4.0. The mean and standard deviations of Heavy metals concentrations (mg/l) in water samples from a hand dug well in mining community compared with National and International standards.

Metal	Metal Conc. (mg/l)	Adefemi and Awokunmi (2010)	NSDW	WHO
Mn	0.985±0.519	ND	NA	0.184[c]
Zn	9.66±0.0791	3.20	3.0 [c]	NA
Pb	16.76±12.23	0.10	0.01 [c]	0.198 [a]
Mg	4.265±0.032	ND	NA	NA
Al	21.06±0.22	ND	0.5 [b]	NA
Cd	0.48±0.08	ND	NA	0.005 [b]
Cr	2.895±0.078	0.02	0.05 [c]	0.5 [a]
Ni	1.19±0.266	0.10	NA	0.02 [b]
Co	3.615±0.971	ND	NA	NA
Cu	1.395±0.026	0.18	NA	NA
Fe	19.072±0.45	0.71	0.30 [c]	0.1 [a]

a Asonye, et al, (2007), b Chukwujindu M.A. I (2010), c. Shalom et al, (2011)
NA means not available

Table 5.0. The mean and standard deviations of Water quality parameters of the water from the site and compared with National and International standards.

Parameter	This study	Aisien et al, (2010)	Nigerian Standard for drinking water	WHO (1993)
Temperature (^{0}C)	19.10±0.01	25.5±2.20		
pH	5.30±0.15	5.18±0.20	6.50-8.50	6.5-8.5
Conductivity (us/CM^{-1})	29.73±0.64	8.01±0.60	1000	
Turbidity (NTU)	1.77±0.00	4.20±1.50	5	5
TDS (mg/l)	96.2±0.13	110.26.70		
Hardness (mg/l)	22.82±2.10	7.00±0.60	150	500
Chloride (mg/l)	14.995±2.98	ND		250
Calcium (mg/l)	17.81±0.82	2.00±0.14	NA	NA
Magnesium (mg/l)	4.265±0.032	5.00±0.65	NA	NA

NA: Not Available

(1.56±0.43) and (0.56±0.83) in gold, columbite and tantalite respectively. Zn (2.67±0.104, 0.06±0.28 and 0.06±0.10) in gold, tantalite and columbite respectively while lead (87.02±1.029, 6.84±0.19 and 0.067±0.39) in gold, columbite and tantalite in a sequential order. It also showed very high Pb in gold confirming that the lead poisoning could be attributed to gold mining in the area. Cr in the solid minerals was (6.165±3.14, 2.15±0.83 and 0.43±0.27) for gold columbite and tantalite while Ni concentration was (15.09±0.17, 0.096±0.82 and 0.08±0.48) for gold, tantalite and columbite respectively. The same trend was obtainable for Cu (1.28±0.065, 0.14±0.01 and 0.067). The actual source of the metals in the solid minerals could be attributed to the background level of metals in soil originating from the parent rock; metals can occur in inert concentrations in soil, however may be converted to mobile forms due to changing environmental conditions or changes in soil properties (Takac et al, 2009). Hence, this research work is suggesting for a speciation of the metals in the soil and the tailings to ascertain the mobile forms of metals in the solid minerals matrix. In relation to the potential risk it is important to know the content of bioavailable forms as well as the properties of soil as this can help significantly to select the measures for reduction of such forms (Takac et al, 2009).

Soil polluted with Hg, Pb, Cu, As and Cr were reported from a gold mining activities, and these metals with higher concentrations were mainly distributed around the gold mills over the studied region. Heavy metals presence in solid minerals and mines tillage have been reported by many authors for example, Ezeaku (2012), evaluated the influence of open cast mining of solid minerals on soil, landuse and livelihood systems in selected areas of Nasarawa state, North-central Nigeria and discovered that the effluents from the mines caused water hardness, the cumulative effects of the pollution lads on the soil and water resources affected the land uses in the host communities. Concas et al, (2006) studied the mobility of heavy metals from tailings to stream waters in a mining activity contaminated site and reported a leaching behavior of the tailings into water bodies through precipitation and desorption. The toxicity of heavy metals has been widely reported. The body chemistry and the simultaneous chemical reactions taking place in the body system catalyze some of these effects. For example, Lead affects children; particularly in the 2-3 years old range leading to the poor development of the grey matter of the brain, thereby resulting in poor intelligence quotient catalysed by Ca and Zn deficiencies (Singh and Kalamdhad, 2011).

In water samples, the heavy metals in water samples revealed high contamination of metals from the mining area especially with metals like Pb (16.76±12.23), Al (21.06±0.22), Cd (0.48±0.08) and Fe (19.072±0.45). The water analysis also revealed the presence of significant amount of essential metals needed for growth and development of the body such as Zn (9.66±0.079) and Mg (4.265±0.032). However, emphasis must be drawn to the fact that the excess of these metals beyond the recommended levels could also trigger the negative effects of other toxic metals like Pb. This high concentration is not surprising due to many factors including soil compositions reported by the same author elsewhere. The total metal concentrations in water revealed a very high concentration of Al (21.06±0.22), this is the most abundant metal on the earth and so the high concentration was not too surprising. However, as reported earlier Fe (19.072±0.45) than both the World Health Organization standard and the Nigerian Standard for Drinking Water as well as the values reported by Adefemi and Awokunmi (2010). Other prominent metals that were higher than the standard limits included Pb (16.76±12.23) that was over one hundred and sixty times higher than both standards and the reported literature.

Understanding the quality of underground water is as important as its quality because it is the main factor determining its suitability for drinking, domestic, agricultural, industrial and touristic purposes (Kaveh et al, 2012). Highly toxic metals such as Cd (0.48±0.08) and Ni (1.19±0.266) were also high and significantly higher than W.H.O. standard suggesting a very high contamination of the water samples. Cadmium is a known toxic metal even at a very low concentration resulting into gastro-intestinal disorder (Okunola et al, 2011). Water quality standards vary from one country to the other. In most developing countries like Nigeria even as there are minimum standards; the standards are not strictly adhered to due to accessibility issues related to water sanitation.

The Anions at certain concentrations are harmful to humans for example; Nitrate and Nitrite are important in human toxicology simply because in the environment it can form nitrogenous compounds by microorganisms present in the soil, water, saliva and even in the gastro intestinal tract. Tantalite was richer in bicarbonate mg/l (7.5), chloride mg/l (420) and sulphate mg/l (268.36) but lower in nitrate mg/l (750) than other solid minerals gold and columbite. Anions were not determined in gold. There was limited literature on anionic compositions of solid minerals. The relative content of a cation or anions is defined as the percentage of the relative amount of that ion to the total cations or anions respectively (Kaveh et al, 2012). The association of nitrate with chloride, calcium and magnesium is an indication that the sources of these ions are anthropogenic. Therefore, the huge release of zinc in waters is as a result of oxidative reaction occurring between sphalerite in tailings and oxygen dissolved in filtering water (Concas et al, 2006).

Physico-chemical properties of water like temperature and pH are important properties that determine the mobility of metals in solution and consequently the water quality. The average temperature of samples (19.10±0.01) in this study was higher the average water temperature of 7.22 for Itaogbolu area of Ondo state reported by Adefemi and Awokunmi (2010) while the average pH (5.30±0.15) in this study was slightly acidic compared to the WHO value and the NSDW. These important parameters (pH and temperature) to some extent determine the mobility of metals in solution. Electrical conductivity is an indicator of water quality and soil salinity (Meindinyo and Agbalagba, 2012). Electrical conductivity of was averagely lower than the values reported by many authors and very insignificant when compared to the national standards.

CONCLUSION

The mineral composition and heavy metals Mn, Zn, Pb, Mg, Al, Cd, Cr, Ni, Co and Cu enrichment of selected solid minerals (Gold, Columbite and Tantalite) in the mining areas of northern Nigeria were assayed. It was observed that the total heavy metals enrichment of the solid minerals were lower compared to those reported in literature except for highly toxic metals Pb and Cd but in the water samples the contamination levels were high in most of the parameters tested. It could be concluded that the source of the contamination of the water samples with those toxic metals (Pb and Cd) could be from some of the solid minerals especially gold.

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