

**TRACE ELEMENT COMPOSITION IN SOLID MINERALS - HEALTH IMPLICATION
IN AN INDISCRIMINATE TAILING DEPOSITION ENVIRONMENT**

Adeseye Muyiwa Arogunjo¹

Department of Physics, Federal University of Technology, P.M.B. 704, Akure, Nigeria

¹Present address: *GSF-Research Center for Environment and Health Institute of Radiation Protection - Medical Physics, Ingolstaedter Landstrasse 1 D-85764 Neuherberg -Munich Germany.*

Abstract

Heavy metals overload taken via ingestion, inhalation and dermal have been found to be detrimental to both the occupationally exposed group and member of the public. The body burden of these metals has been a source of concern in environmental safety regulatory programs. The risk factor becomes potentially high in an environment where regulatory safety criteria are either neglected or not available. The indiscriminate or unregulated mining activities in Nigeria have been a point of concern to public health. In view of the potential toxicological and radiological health hazard posed to the environment due to mining activities in Nigeria, Solid mineral ores (iron, tin and tantalite) from south-western and north-central (Kogi and Ekiti States) of Nigeria were analysed for their trace-metal contents in order to evaluate their potential environmental hazards. The samples were found to contain some major, minor and trace elements of varying concentrations. The elements reported here are K, Ca, Ti, V, Cr, Mn, Fe, Ni, Sr, Y, Zr, Nb, Sn, Ta, Re, Th, U, Sc, Cd, Bi, Ra and Zn. The presence of toxic metals in the mineral ores calls for caution and make occupational and public toxic protection programme inevitable. The possible pathway into the food chain as a result of mining activity has also been presented.

Keywords: heavy metals; natural radionuclide; contamination; mineral ore; public health.

Introduction

Heavy metals are natural constituents of the Earth's crust, but human activities have drastically altered their geochemical cycles and biochemical balance (Giachetti and Sebastiani, 2006). Mining activities all over the world have contributed immensely to this observed disequilibrium and therefore affect the terrestrial ecosystem due to the excavation of large amount of sand and the eventual accumulation of large volume of tailings. Mining activities causes' serious environmental impact like the destruction of natural soil and the extraction of important volumes of materials and elevated levels of trace elements are frequently common characteristics of most mining tailings (Vega et al, 2004). Several environmental heavy metal pollution is caused mainly by emissions from cement and oil industries (Nyarko et al, 2006). Although heavy metals are released in varying quantities into the soil from parent materials, increasing environmental contamination has been caused by human activities, such as mining, smelting, fossil fuel combustion, agricultural practices and waste disposal and extraction of metal ore causes generally a multi-elemental contamination of the environment (Remon et al, 2005; Perry et al, 2005; Adamo et al, 2003; Banat et al, 2005; Akinlua et al, 2006; Birkefeld et al, 2006). These tailings usually contain high concentrations of heavy metals and the irreclaimable reagents and chemicals used in the extraction processes, which tend to increase the natural metal content of the soil. Heavy or toxic metals are trace elements that are non bio-degenerate and indiscriminate dumping of tailings from mining sites will lead to bioavailability and bioaccumulation in the soil, surface water and natural vegetation. The most critical effects of this pollution occur when toxic waste accumulates in farmlands. High concentration of these metals in soil may cause long-term risk to ecosystems and humans (Querol et al, 2006). Food crops grown on such land accumulate toxic

metals, which find their way into the food chain. The health risk to human become very high from heavy or toxic metal exposure either by direct inhalation of suspended dust particles in air and dermal contact or indirect ingestion through consumption of food crops grown in tailing enriched land. Although the body need some trace elements for proper functioning, there are however, some toxic metals that interfere with enzyme systems and metabolism of the body. Heavy metal overload is detrimental to the body, accumulation on the wall of coronary arteries impede normal blood flow and hence increase the probability of cardiovascular blockages. Heavy metal inhalation may result in serious health effect, normal functioning of the immune system may be compromised considerably. In most mining sites in Nigeria, unregulated mining activities have been operational leading to indiscriminate dumping of industrial waste. Agricultural practices have been the main occupation of inhabitants around the mining area. The main staple foodstuff grown in the area like root tubers, cereal and vegetables are being irrigated from streams and dams in the mining sites. The dams and streams also serve as domestic drinking water for the inhabitant of the area. Heavy metals have been found in foodstuff and have a potential health hazards to man through the dietary pathway in Nigeria (Obiajunwa et al, 2001). It has been observed that mining, milling and processing of mineral ore enhance heavy metal body burden not only to the mine workers but also to the inhabitants of the mining and processing sites. This enhanced toxicity posed by these practices remains a source of concern in both occupational and public toxic protection programs. In view of the serious hazards posed to man, especially through the ingested and inhalation pathway, their concentration and disposition pattern cannot be neglected in order to properly access the overall body burden. This work is aim at identifying and characterising heavy metal composition in pollution source

target, comparing the pollution level from mining industries into the environment and setting up possible incorporation pattern to the inhabitants around the mining sites.

Geology of the Sampling Sites

The study area lies within the Nigerian basement complex with three broad lithological groups. The poly-metamorphic migmatite gneiss of various compositions, the low-grade sediment dominated schist and the sync-tectonic to late tectonic granitic rock of varying compositions. Two distinct provinces can be distinguished in this basement complex, the Western which is characterised by narrow low grade schist belt and the Eastern which comprises mostly migmatites, granites and Mesozoic young granites. The South-western Nigeria is a part mostly recognised by five major groups of rocks: the migmatite-gneiss complex which comprises quartzite, quartz schist and small lenses of calc-silicate rocks; the slightly migmatized to unmigmatized paraschists and meta-igneous rocks which consist of poly-tectonic schist, quartzite amphibolites, talcose rocks, meta-conglomerates, marbles and calc-silicate rocks; charnockitic rock; older granites, unmetamorphosed dolerite dykes believed to be the youngest. The migmatite-gneiss complex is thought to have resulted from a complex association of deformative shearing and folding, and granitisation and migmatitisation processes. The slightly migmatized to unmigmatized Para schist represent a sedimentary cover on the gneiss-migmatite complex. Iktape where iron ore was collected is within the Okene migmatite complex in the South-central Nigeria and the deposit is described as a hematite-magnetite quartz body in a ferruginous quartzite type. The Kabba area where tin and tantalite is found is within the undifferentiated schist belt of Igara and Kabba-Jakura formation. This is part of the most Easterly schist belts in the South-western Nigeria distributed around the Okene Migmatic nucleus. There is no geochronological evidence available for the age of this

belt, but there are diverse structural trends and association with Pan African granites which suggested a Kiboran age. The Ijero tin, Ilukun tantalite and Ipoti iron ores fall within the polydeformed schist of South-western Nigeria. The schist belt in this area is extremely poorly exposed because of tropical climate conditions and rainforest vegetation.

Materials and Methods

Sample collection and preparation

Mineral ore samples were collected from mining sites in Ekiti and Kogi states in the South-western and central part of Nigeria, respectively. Tin and tantalite ores were collected from Kabba and iron ore sample from Itakpe in Kogi state. Tin, tantalite and iron ores were collected from Ijero, Ilukun and Ipoti in Ekiti state, respectively. The samples were collected in clean polyethylene bags for transportation to the laboratory. Prior to analysis, all samples were sun-dried, pulverised and homogenised by grinding into fine powder in an agate mortar. The samples and the standard were pressed into thick pellets of about 13 mm diameter in Spec-Caps (Obenauf, 1991) without the aid of a binder ready for analysis.

Analysis

A Siemens FKO-04 tube type EDXRF spectrometer with Mo anode of a Kristalloflex 710H X-ray generator was employed in this work. The spectrometer made use of a Canberra series 7300 Si (Li) detector with a resolution of 165 eV at 5.9 keV, a Canberra series S 100 MCA card interfaced to a PC with a Canberra model 1510 integrated signal processor. The equipment operates under quantitative X-ray analysis system (QXAS) (QXAS, 1993) with data acquisition, spectrum and

quantitative analysis and interpretation software. The samples and standards pellets were irradiated separately for 20 min at fixed tube operating conditions of 30 kV and 5 mA. The unfiltered Mo - $K_{\alpha, \beta}$ excitation allows determination of elements with characteristic K- and L- lines in the energy region of 3.3 – 16 keV (Obiajunwa et al, 2002). The smooth-filter model in the AXIL program of QXAS package was used to filter the spectra over the energy region of interest. The accuracy and precision of the analytical technique was performed using geological standards LINK Analytical Profile Reference standards by analysing the Bureau of Analysed sample LTD Standard Reference Material: BCS-CRM No. 355 (Tin Ore).

Results and discussion

The results of the elemental characterisation of some mineral ores mined in Nigeria using EDXRF have been presented. The concentrations of the various elements found in tin ore from two mining sites (Kabba and Ijero) are presented in Table 1. Thirteen elements (K, Ca, V, Mn, Fe, Ni, Sr, Y, Sn, Ta, Re, Th, and U) were found in tin ore from Kabba mining site while Fifteen elements (K, Ca, V, Mn, Fe, Ni, Sr, Y, Zr, Nb, Sn, Ta, Re, Th, and U) were found in the sample from Ijero mining site. The concentrations of the various elements in Iron ore from two mining sites are given in Table 2. Six elements (Ti, Cr, Mn, Fe, Ta and Ca) were found in the sample collected from Itakpe while nine elements (Sc, Ti, Cr, Mn, Fe, Cd, Ta, Re, Ca and Bi) were present in the sample from Ipoti. The elements found in tantalite ore from Kabba mining site were presented in Table 3, a total of eleven elements (Ca, Ti, V, Cr, Mn, Fe, Zr, Nb, Cd, Ta and Ra) were found in the sample. It should be noted that Ti and Cr were not found in tin ore samples from both mining sites presented in Table 1 while Zr and Nb found in the same sample from Kabba were not present in the sample from Ijero and Ca found in large quantity in the sample from Ijero was found

in trace quantity in the sample from Kabba. The difference in the elemental composition of tin samples from the two locations could be attributed to different chemical form (speciation) of tin compound. In the case of iron ore presented in Table 2, the above mentioned reason could be adduced as to why Sc, Cd, and Bi found in the sample from Ipoti are not present in the sample from Itakpe, Ca in the sample from Itakpe is not present in the sample from Ipoti and Ti found in significant proportion in the sample from Itakpe was found in trace proportion in the sample from Ipoti. It is also worthy of note that iron ore presented in Table1 has the greatest elemental composition when compared with other mineral ore samples analysed. Iron is the most abundant metal on Earth, and is believed to be the tenth most abundant element in the universe. It is also the second most abundant (by mass, 34.6%) element making up the Earth; the concentration of iron in the various layers of the Earth ranges from high at the inner core to about 5% in the outer crust. Tantalite-columbite or tantalite-niobium ores are oxides of tantalum, niobium oxide, iron and manganese $(\text{Fe,Mn})(\text{Ta,Nb})_2\text{O}_6$. The primary elements of interest in this work are the heavy or toxic metals of Ni, Cd, and Cr, which are of toxicological importance to human health. Nickel was found in tin ore with concentration ranging from 410 – 680 mg kg^{-1} , Cadmium was detected in trace quantity ($6.14 \pm 1.05 \%$) in iron ore from Ipoti and in large quantity ($5170 \pm 126 \text{ mg kg}^{-1}$) in tantalite ore from Kabba and Chromium value ranged 800 – 2300 mg kg^{-1} in iron ore samples from Ipoti and Itakpe mining sites and has a of 340 mg kg^{-1} in tantalite ore from Kabba. Cadmium was not detected in tin ore from the two mining sites sampled. The three heavy metals commonly cited as being of the greatest public health concern are cadmium, lead, and mercury. There is no biological need for any of these three heavy metals. Cadmium has many commercial applications, including electroplating and the manufacture of batteries. Cadmium enters air from mining industry, burning coal and

household wastes. Cadmium particles in air can travel long distances before falling to the ground or water. It enters water and soil from waste disposal and spills or leaks at hazardous waste sites. It binds strongly to soil particles. Some cadmium dissolves in water. It doesn't break down in the environment, but can change forms. Fish, plants, and animals take up cadmium from the environment. Cadmium stays in the body a very long time and can build up from many years of exposure to low levels. Exposure to cadmium can occur in the workplace or from contaminated foodstuffs and can result in emphysema, renal failure, cardiovascular disease, and perhaps cancer (www.tuberoze.com). In view of the deleterious health hazards posed by the incorporation of these heavy metals into the natural ecosystem, it is worthy of note that the indiscriminate dumping of mine tailings by these mining industries will undermine public health. As at present, little or no data is available as to the tolerance levels of heavy metal in Nigeria environment. Majority of the inhabitants of the mining communities are peasant farmers and large scale agricultural practises like food crops cultivation is on the increase. The same farmland used for crop production also serves as repository for waste generated from the proximate mining industries. The Federal Environmental Protection Authority (FEPA) in the country as at present has no standard value for both occupational and public tolerance limits of exposure to these heavy metals. In order to enumerate the seriousness of this matter, possible heavy metal incorporation pattern into the food chain and eventually to the member of the public is presented in Fig 1. The figure presents the various possible pathways by which the member of the public could have contact with toxic metals as a result of mineral ore mining activities in an unguided tailing deposition environment.

Conclusion

The elemental compositions of some mineral ores mined in Nigeria have been presented in this work using the EDXRF analytical technique. Heavy metals of varying concentrations were found in the mineral ores (Iron, Tin and Tantalite) sampled. Heavy metals of environmental and public concern were also detected and the implications to the natural ecosystem and human health have been enumerated. Possible heavy metal pathway model into the food chain has been developed for easy assessment of contamination in the environment. The lack of appropriate reference standards necessary to assess and re-assess environmental pollution as a result of human activities, and the presences of toxic metals like Ni and Cd calls for caution and make occupational and public toxic protection programme inevitable. The possibility of both public and occupational exposure to these toxic metals by inhalation, ingestion and dermal also make proper management of waste products from mining industries in Nigeria very important.

Acknowledgements

The author recognised the contribution of his post graduate diploma students (Ilesanmi. R.; Ogunmade, F.; Adeleke, O.) for their involvement in the sample collection toward the award of PGD in the Department of Physics, Federal University of Technology, Akure. Many thanks to the Alexander von Humboldt foundation for granting the fellowship that enables unlimited access to internet facility used for the final preparation of this manuscript at the GSF-Research Center for Environment and Health Institute of Radiation Protection - Medical Physics, Munich Germany.

Reference

1. Giachetti, G. and Sebastiani, L., 2006. Metal accumulation in poplar plant grown with industrial waste. *Chemosphere* 64, 446 - 454.
2. Vega, F. A., Covelo, E. F., Andrade, M. L., Market P., 2004. Relationships between heavy metals content and soil properties in minesoils. *Analytica Chemical Acta* 524, 141 - 150.
3. Nyarko, B. J. B., Adomako, D., Serfor-Armah, Y., Dampare, S. B., Adotey, D., Akaho, E. H. K., 2006. Biomonitoring of atmospheric trace element deposition around an industrial town in Ghana. *Radiation Physics & Chemistry* 75, 954 - 958.
4. Remon, E., Bouchardon, J. L., Cornier, B., Guy, B., Leclerc, J. C., Faure, O., 2005. Soil characteristics, heavy metal availability and vegetation recovery at a formal metallurgical landfill: implication in risk assessment and site restoration. *Environmental Pollution* 137, 316 - 323.
5. Perry, P. M., J. Pavlik, W., Sheets, R. W., Biagioni, R. N., 2005. Lead, cadmium, and zinc concentrations in plaster and mortar from structures in Jasper and Newton Counties, Missouri (Tri-State Mining District). *Science of the Total Environment* 336, 275 - 281.
6. Adamo, P., Denaix, L., Terribile, F., Zampella, M., 2003. Characterization of heavy metals in contaminated volcanic soils of the Solofrana river valley (southern Italy). *Geoderma* 117, 347 - 366.
7. Banat, K. M., Howari, F. M., Al-Hamad, A. A., 2005. Heavy metals in urban soils of central Jordan: should we worry about their environmental risks? *Environmental Research* 97, 258 - 273.

8. Akinlua, A., Ajayi, T. R., Adeleke, B. B., 2006. Preliminary assessment of rare earth element contents of Niger-Delta oils. *Journal of Applied Sciences* 6, 11 - 14.
9. Birkefeld, A., Schulin, R., Newack, B., 2006. In situ investigation of dissolution of heavy metal containing mineral particles in an acidic forest soil. *Geochimica Et Cosmochimica Acta* 70, 2726 - 2736.
10. Querol, X., Alastuey, A., Moreno, N., Alvarez-Ayuso, E., Garcia-Sanchez, A., Cama, J., Ayora, C., Simon, M., 2006. Immobilization of heavy metals in polluted soils by the addition of zeolitic material synthesized from coal fly ash. *Chemosphere* 62, 171 – 180.
11. Obiajunwa, E. I., Johnson-Fatokun, F. O., Olaniyi, H. B., Olowole, A. F., 2001. Analysis of some Nigerian solid mineral ores by energy-dispersive X-ray fluorescence spectroscopy. *Nucl. Instr. & Meth. In Phy. Research B* 184, 437 - 440.
12. Obenauf R. H., (Ed), *Spex Handbook of Sample Preparation and Handling*, 3rd Ed, (1991) 95.
13. *Qxas Users Manual*, IAEA, Vienna, 1993.
14. Obiajunwa, E. I., Johnson-Fatokun, F. O., Olaniyi, H. B., Olowole, A. F., 2002. Determination of the elemental composition of aerosol samples in the working environment of a secondary lead smelting company in Nigeria using EDXRF technique. *Nucl. Instr. & Meth. In Phy. Research B* 194, 65 - 68.
15. WWW.TUBEROSE.COM/HEAVYMETALTOXICITY.HTML.