Ascertaining the Potential of Lead Mobilisation into the Geo-environment by Spent Fire Assay Crucibles

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Abstract

During fire assaying of gold, litharge (PbO) is a component of the flux that is used to produce the matte that collects the gold. The spent crucible always contains residual lead (Pb). Unfortunately, the spent crucible is disposed in landfills. When the lead weathers, the lead is mobilised into the geo-environment. This research was conducted to ascertain the chemical composition and mobility of lead in the spent crucibles. An X-Ray Fluorescence (XRF) was used for the determination of the spent crucible composition and the mobility was studied by leaching, using rainwater as lixiviant. The XRF analysis showed that Silicon (up to 59.02 %) and Aluminium (up to 33.18 %) are the main components of the crucibles while lead (up to 1.6 %) was found to be a minor inclusion. The study further revealed that, spent crucibles contain lead that can be mobilised into the geo-environment during storage.

Keywords: Fire Assay, Characterisation, Crucible, Mobilisation and Lead

1 Introduction

Extraction of gold from its ore comes with different processes which include; exploration, mining and mineral processing. Samples taken from exploration mine site are tested using fire assay procedure to determine the grade of the ore.

At the end of the fire assay process, slags, cupels and crucible wastes are generated. In most assaying laboratories, litharge (PbO) is an important flux added to the assay samples. The litharge (PbO) decomposes and lead (Pb) is formed as a product. This lead (Pb) collects the precious metal during crucible fusion. However, some of the lead is absorbed by the crucibles in the assaying process.

In Ghana, the fire assay wastes generated are either collected by waste management companies for treatment or are disposed in un-engineered landfills. When these crucibles are landfilled, the lead contained in the crucible waste can be leached into the soil during rainfall. The lead is taken up by plants as soil nutrient and also, may seep into underground water. Lead in this form when taken by human through food chain and water they drink causes skin rashes, liver damage, respiratory diseases, even death and other effects on the environment (Demayo *et al.*, 1982; Tong *et al.*, 2000; Zhang *et al.*, 2012; Daley *et al.*, 2018). For such reason, there have been several reports in literature discussing gold analysis by fire assay method and emphasizing more on how to reduce the amount of lead-containing waste in the environment (Resano *et al*., 2006; Balaram, 2008; Berdnikov *et al.*, 2010).

This research therefore seeks to characterize spent fire assay crucibles and also ascertain lead mobility from spent fire assay crucibles into the geo-environment by rainwater

2 Materials and Methods Used

2.1 Sampling

Unspent and spent crucibles were collected from an Assay Laboratory in Ghana. Seven out of fifty (50) spent crucibles were selected with simple random sampling method to obtain 5.0 kg of the material. Also, with simple random sampling, three of 30 unspent crucibles (2 kg) were selected. The sampled crucibles were sent to the laboratory for sample preparation and further analysis.

2.2 Sample Preparation

After sampling, both spent and unspent crucibles were crushed using a primary jaw crusher (Terminator – 9833) to a particle size range of 80 % passing 2 mm. The samples were further pulverized (using ESSA Australian Ltd, Yellandway Dassendean – 6054 Pulverizer) to obtain a particle size range of 80 % passing 38 µm for further analysis.

2.3 X-Ray Fluorescence (XRF) Analysis

To prepare samples for XRF analysis, 0.9 g of CereoxLicowax, BM-0002-1 was added as a binder to 4 g of each set of samples (spent and unspent). Samples were put in dies, homogenized at a frequency of 20 Hz for 2 mins with a Retsch-MM 301 Homogenizer. The samples were then put in new dies sealed and a Specac hydraulic press was manually operated to obtain pellets of 32 mm in diameter. The pellets were put in the calibrator of an XRF and tested for elemental composition.

2.4 Leaching Experiment

A pH test was first carried out on the rainwater. Samples of 20 g of crucible waste (particle size ≤ 38 µm) were transferred into 7 beakers. Adding 60 ml of rainwater, the samples were leached for a period of 8 days (0.5 hr, 1 hr., 3 hrs, 24 hrs, 72 days, 120 hrs and 192 hrs). Liquid to solid ratio of 3:1 was used. After each time, the samples were filtered and centrifuged. The pH of each filtrate was measured. The filtrates were subjected to chemical analysis using an Atomic Absorption Spectrometer (AAS – AA400P).

3 Results and Discussion

3.1 pH of Rainwater

The pH of the rainwater used for leaching the spent crucible was in the range; 5.95–5.99. The rainwater can therefore be described as being slightly acidic.

3.2 Head Grade Analysis

Table 1 shows results of the chemical composition of both the spent and unspent crucibles using XRF. The major constituents of the unspent crucible are Silicon and Aluminium. Potassium, Iron and Calcium are in minor quantities whereas Titanium, Zircon and Lead are in trace amounts. This finding is similar to results of characterisation of crucibles obtained by Martinón-Torres *et al.* (2003) and (2008) respectively. The presence of lead in the unspent crucible may be attributed to mineralogy of the raw materials used in manufacturing the crucible. Chemical analysis of the spent crucibles shows that approximately 1.6% of lead is incorporated into the crucible after crucible fusion. This shows that there is an appreciable amount of the lead that may be released into the geo-environment if this spent crucible is not properly disposed.

Table 1 Chemical Analysis of Crucible Waste Using XRF

Elements Present	Unspent Crucible (ppm)	Spent Crucible (ppm)	Unspent crucible (wt %)	Spent Crucible (wt %)
Silicon (Si)	376537	281946	74.46	59.02
Aluminium (Al)	95130	158519	18.11	33.18
Potassium (K)	16756	7582	3.31	1.59
Iron (Fe)	11480	8451	2.27	1.77
Lead (Pb)	**159**	**7679**	**0.03**	**1.61**
Calcium (Ca)	5249	5249	1.04	1.10
Titanium (Ti)	1896	4701	0.37	0.98
Sulphur (S)	0	2767	0.00	0.58
Zircon (Zr)	115	327	0.02	0.07

3.3 Leaching Experiment

Figure 1 shows the results of leaching the spent crucible with rainwater for a period of eight days. From the graph, there is a general increase in the amount of lead mobilised with time. The lead concentration started increasing appreciably with time at the 3rd hour where a lead concentration of 0.006% (0.43 mg/L) of the total lead available was recorded. The concentration increased gradually to 0.13% (10 mg/L) on the eighth day. This concentration exceeds the recommended limit (0.1 mg/L) for lead in effluent by the Ghana Environmental Protection Agency (GEPA, 2018). Therefore, toxic levels of lead can easily be mobilised into the geo-environment.

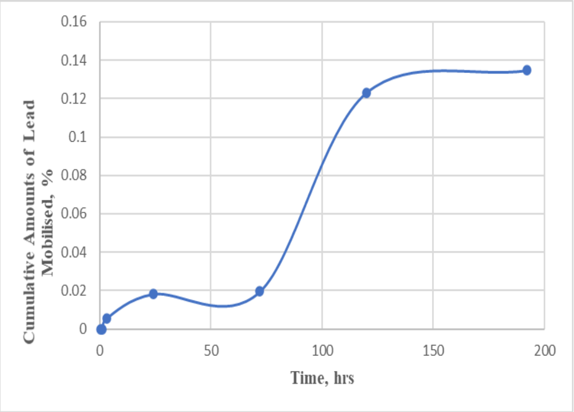

Figure 1 A Graph of Amount of Lead Mobilised with Time

3.4 pH Test

Table 2 presents the results of the pH tests conducted on the leachates. The pH values of the leachate increased with time and were higher than that of the lixiviant or the leaching medium (rainwater, 5.98). The pH values of the leachate were relatively constant at 9.2 – 10.16 indicating that the leachate was alkaline in nature. The alkalinity may be attributed to the high level of calcium in the spent crucible being released during the leaching process.

Table 2 pH Results of Crucible Leachate

Time (Hour)	pH
0.5	9.27-10.16
1	9.60-9.68
3	9.69-9.80
24	9.61-9.90
72	9.54-9.90
120	9.60-9.85
192	9.54-9.64

3.5 Comparison of Lead Concentration with Ghana Standards

From the sector of specific effluent in Ghana (GEPA, 2018), the maximum level of lead concentration in effluent is specified as 0.1 mg/L and pH 6-9. Lead has been one of the widely used chemicals in the assaying laboratory. It is used in different forms and in large quantities hence the results of this study can be compared with the Ghana effluent standard. Consequently, the lead concentration leached out from the waste crucibles obtained from the laboratory exceeded the acceptable levels for lead. Therefore, there is a high risk of contaminating the geo-environment if spent crucibles from fire assay laboratories are not properly managed.

4 Conclusions and Recommendations

4.1 Conclusions

From the results and discussion, it can be concluded that;

- Aluminium and Silicon are the main components of both the spent and unspent crucibles.
- Lead is a major contaminant of spent crucibles from fire assay laboratories.
- The leachate from the crucible-rainwater leaching has an alkaline pH between 9.2 - 10.16 and exceeds the maximum limit specified by Ghana EPA standards of 6-9.
- Lead mobility from spent crucibles in rainwater increases with increasing leaching time.
- A maximum concentration of 0.13 % (10 mg/L) of lead was mobilised by rainwater within eight (8) days of the study and exceeds the Ghana EPA recommended limit of 0.1 mg/L.

4.2 Recommendations

It is recommended that,

- Mineralogical analysis on the crucibles to be conducted to ascertain the mineral phases present.
- The effect of spent crucible particle size on lead mobilisation be ascertained.

References

Balaram, V. (2008), "Recent advances in the determination of platinum group elements in exploration studies-A review", *Journal of the Geological Society of India*, Vol. 72, No. 5, pp. 661 – 677.

Berdnikov, N., Balaram, V., Cherepanov, A., Avdev, D., Konovalova, N. and Sukharulidze G. (2010), "Some observations on the determinations of platimun group elements and gold in black shales", *Current Science*, Vol. 99, No. 4, pp. 518 – 521.

Daley, G.M., Pretorius, C.J. and Ungerer, J.P. (2018), "Lead Toxicity: an Australian Perspective", *Clinical Biochemist Reviews*, Vol. 39, No. 4, pp. 61-98.

Demayo, A., Taylor, M.C., Taylor, K.W., Hodson, P.V. and Hammond, P.B. (1982), "Toxic effects of lead and lead compounds on human health, aquatic life, wildlife plants, and livestock", *Critical reviews in environmental science and technology*, Vol. 12, No. 4, pp. 257-305.

Ghana Environmental Protection Agency (GEPA) (2018), (Standards for Industrial/facility

Discharges into Water Bodies and Water Courses, Standards for Air Quality and Standards for Noise) Regulations 20, pp.14.

Martinón-Torres, M. and Rehren, T., 2003. Ceramic materials in fire assay practices: a case study of 16th-century laboratory equipment. In Understanding People through their Pottery. Proceedings of the 7th European Meeting on Ancient Ceramics (EMAC '03), Lisbon, pp. 139-149.

Martinón-Torres, M., Freestone, I.C., Hunt, A. and Rehren, T. (2008), "Mass-Produced Mullite Crucibles in Medieval Europe: Manufacture and Material Properties", *Journal of the American Ceramic Society*, Vol. 91, No. 6, pp. 2071-2074.

Resano, M., Garcia-Ruiz, E., McIntosh, K. S., Hinrich, J., Deconick, I. and Vanhaeckea F. (2006), "Comparison of solid sampling techniques laser ablation-ICP-MS, glow discharge MS and spark-OES for the determination of pltinum group metals in Pb button obtained by fire assay of platiniferous ores", *Journal of Analytical Atomic Spectrometry*, Vol. 21, No. 9, pp. 899 – 909.

Zhang, X., Yang, L., Li, Y., Li, H., Wang, W. and Ye, B. (2012), "Impacts of lead/zinc mining and smelting on the environment and human health in China", *Environmental monitoring and assessment*, Vol. 184, No. 4, pp.2261-2273.

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