

Determination of best processing route for lead recovery from fire assay slags

Bennetta Koomson¹, John A. Koomson^{1,*}, Prince D. Appiah¹, Benedictus K. Orison¹, Kwasi K. Anweasu¹

Received: 14th February, 2023 / Accepted: 29th October, 2024

Published online: 5th December, 2024

Abstract

In Ghana, voluminous amounts of slags are generated by fire assay laboratories. Since lead is a major constituent in fire assay slags, there is a possibility of lead finding its way into the slag matrix and being released into the geo environment upon disposal. This work ascertains the possible amount of lead in the slags and recovers it using flotation, gravity concentration and acid-leaching methods. The initial samples were chemically characterized using an X-ray fluorescence (XRF) and acid-digested for Atomic Absorption Spectroscopy (AAS) analysis. The results indicate that fire assay laboratories have elevated heavy metal concentrations especially lead (Pb), which is above the Ghana Environmental Protection Agency (GEPA) and World Health Organization (WHO) permissible levels, demonstrating anthropogenic impacts. From the study, the recoveries were found to be 77.83 %, 77.09 % and 75.90 % for flotation, gravity separation and acid leaching respectively. It is concluded that the gravity separation method is the best processing route for lead recovery from fire assay slags since the gravity separation poses little or no environmental dangers whereas flotation and acid leaching processes require chemicals that can cause skin irritation and other adverse effects. Also, the gravity separation process requires less time to perform.

Keywords: Fire Assay Slag, Flotation, Gravity Concentration, Acid-leaching

Introduction

Gold is one of the main minerals that contribute significantly to the economic development of Ghana. The Gold content in most of the mining areas is around 3 g/t and those ores offering 10 g/t are considered to have the best quality (Asner *et al.*, 2013). Because of the low contents, the extraction of gold is a costly process involving very expensive technologies, high energy input and skilled labour. The cost of the exploration and extraction process is raised even more as the gold becomes scarce (Henckens *et al.*, 2016). This results in a lower limit on the ore grade from which the gold can be extracted profitably. Hence, the precise quantification of gold in the ores is important for determining the economic viability of the overall operation.

The lead fire assay test is known to be the most conclusive and reliable method for the quantification of gold in the ores (William, 2006). This method allows for a high level of pre-concentration before analytical quantification, as well as a very exact and accurate gold determination (Cerceanu *et al.*, 2016). The pulverized sample is weighed and combined with fluxing agents such as soda, borax, and silica in the first stage. The fluxing agents aid the separation of the precious metal from the gangue. Lead (Pb) is added to the flux as a collector. The sample is then heated in a furnace to a temperature of 1000 – 1100 °C to fuse and isolate the collector material “button” which contains the valuable metals. After 20 minutes, the sample is withdrawn and allowed to cool, forming a mixture of Pb with all of the Gold (Au) and Silver (Ag) present in the sample called a ‘lead button’, as well as a molten slag made up of flux and other mining wastes. In the second stage, named cupellation, the precious metals are extracted from the lead button. Cupellation is a high-temperature oxidation process where the Pb and other base metals such as Copper in the lead button are converted into oxides. The Pb oxidizes and is absorbed into the cupel leaving a precious metal bead. This bead is then dissolved in aqua regia for analysis which can be carried out by different analytical techniques (Michaud, 2016).

Slag is the glass-like leftover after separating the desired metal from the raw ore. In Ghana, a typical fire assay laboratory generates about 50 tons of slags annually. The slag

made in fire assay is usually a mixture of metal oxides and silicon dioxide (Anderson, 2018). During the fusion stage, lead might find its way to the slag matrix. As a result, the slag becomes contaminated with heavy metals, making its disposal undesirable to life. Therefore, developing methodologies for recovering lead from such wastes is critical for minimizing environmental risks and allowing lead to be reused, as well as meeting the industrial need for lead compounds.

Both pyrometallurgical and hydrometallurgical methods can be used to recover lead from these wastes. Because pyrometallurgical procedures typically emit SO_x gases and particulates of lead into the atmosphere, resulting in huge amounts of hazardous waste; an increasing number of researchers have concentrated on the development of more ecologically friendly hydrometallurgical and electrochemical processes for extracting lead and other harmful metals from wastes (Khaliq *et al.*, 2014).

This work sought to transform hazardous fire assay slag into non-hazardous materials by recovering the lead in the process using flotation, gravity separation and acid leaching. The products after the various experiments were analyzed to determine the percentage of lead recovered.

Materials and Methods

Sampling and sample preparation

Fire assay slag samples were collected from an assay laboratory in Kumasi, Ghana. Five spots were identified and collected using a random sampling method from the slag deposition area with a shovel. The sample was crushed using a primary laboratory crusher (*Terminator 9833*). The crushed sample was homogenized and divided into two parts using a riffle splitter. The sample was then pulverized using a pulveriser (*ESSA 82000 0047 7035*) to a particle size of -75 µm.

Chemical characterization of the fire assay slags

X-ray fluorescence and x-ray diffractometry analyses

An amount of 4 g of pulverized fire assay slag (-75 µm) was weighed by an Adventure Pro AV 264 electronic balance. To prepare the sample for XRF analysis, 1.0 g of Corohicowax, BM-0002-I was added as a binder to the pulverized sample and weighed with a balance again. The sample was then mixed thoroughly using a RETSCH MM 307 homogenizer in a sample cup. The sample was then transferred into a die and placed in a specific hydraulic press machine to mould the

*Corresponding author: johnkoomson332@gmail.com

¹Materials Engineering Department, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana

mixture into a coin-shaped pellet. The pellet produced was then placed in the Vanta workstation test chamber of Olympus VMR, 2018 XRF Machine. The XRF machine operates by shooting X-rays onto the mounted pellet to give feedback. After shooting, the result obtained was read via Olympus 3.12.34 software on a computer.

The mineralogical composition of the slag sample was determined using a Bruker XRD (Advance D8). The device was operated at 40 kV and 40 mA. The wavelength of the Cu K α radiation $\lambda = 0.1541$ nm. At a step size of $0.02^\circ/\text{min}$, scanning was performed for 2θ values between 10° and 80° .

Acid digestion test using aqua regia

Twenty grams (20 g) of powdered fire assay slag samples (-75 μm) was weighed in a glass mixing container. A mixture of HCl and HNO₃ acids was used to dissolve the sample. This mixture was prepared in a fume chamber by following the standard aqua regia procedure with mole ratio (HCl: HNO₃) = 3:1. The acid mixture was poured into the glass mixing container containing the sample and swirled to ensure an even mixture. In the fume chamber, the solid-liquid mixture obtained was placed on a hot plate and allowed to heat at a temperature of 150°C for 45 minutes. In addition to the heating, the solution was stirred to increase the rate of reaction. After heating, the solid-liquid solution was filtered, and the filtrate was cooled before being analyzed using Atomic Absorption Spectrometer analysis.

Gravity separation

Five hundred grams (500 g) of pulverized sample of fire assay slags was introduced in the form of slurry into the unit through a central tube. The centrifugal force causes the feed solids to fill the inter-riffle spaces from top to bottom. Once these spaces are full of solids, the introduction of further feed starts the sorting stage where heavy minerals displace the lighter minerals and as a result, the heavy minerals are trapped in the inter-riffle spaces while the lighter ones are carried by water to the bottom of the unit, hence a separation occurs. Both the concentrate and tails were dried, weighed (and recorded) and chemically characterized using AAS analysis.

Flotation test

Flotation tests were done using a Denver D12 Laboratory Machine. Two hundred grams (200 g) of the slag sample was used at a pulp density was 17%. Pine oil and Potassium amyl Xanthate (PAX) were used as frother and collector respectively. The impeller speed and oxygen flow rates were 1100 rpm and 4–5 L/min respectively. The conditioning times given for pulp and collector were 10 minutes and 5 minutes respectively. The concentrate and tailings obtained were dried and weighed. To determine the percentage recovery, the concentration of lead in the concentrate was determined by acid digestion and analyzed using Atomic Absorption Spectrometry (AAS).

Leaching process

Fifty grams (50 g) of -75 μm pulverized fire assay slags were transferred into a leach bottle. 1M acetic acid solution was prepared and added to the sample in the bottle. The sample was placed on a bottle roller at about 80 rpm. The experiment was performed at room temperature and a pressure of 1 atm for 24 hours. The leachate samples were filtered and AAS analysis was performed to determine the concentration of lead present.

Results and Discussion

Characterization of fire assay slags

The chemical characterization of the fire assay slag was determined using X-ray fluorescence, and the results are presented in Table 1. From this table, it can be deduced that

the major elements present in the fire assay slag are Lead (Pb) and Silicon (Si). The results indicate that fire assay laboratories have elevated heavy metal concentrations especially lead (Pb) which is above the Ghana Environmental Protection Agency (GEPA) and World Health Organization (WHO) permissible levels; demonstrating anthropogenic impacts (Armah et al., 2010) if not well disposed. The findings justify the concern over the disposal of fire assay slags and emphasize the importance of developing and implementing a methodology for eliminating lead from the slag.

Table 1 XRF analysis results

Element	Concentration (ppm)
Sn	2863
Cd	3052
Al	4345
Ca	5098
K	5369
Si	49564
As	5797
Fe	9366
S	25677
Pb	149983
Others	1127

The X-ray diffraction spectrum of the fire assay slag is shown in Figure 1. The results confirm the presence of lead in its oxide state, identified as litharge (PbO). The presence of litharge (PbO) can be attributed to unreacted PbO added during the crucible fusion process of fire assay. The pattern also reveals the poor crystallinity of the slag sample, thus confirming the glass-like nature of fire assay slags. This result compares with the work done by Bazan *et al.* (2015)

Gravity concentration technique

Results obtained from Gravity Concentration are shown in Table 2. Gravity concentration is a low-cost physical technique that separates minerals of different densities based on their relative movement in reaction to gravity and the resistance to motion provided by a viscous fluid. A substantial density differential between the mineral of interest and the

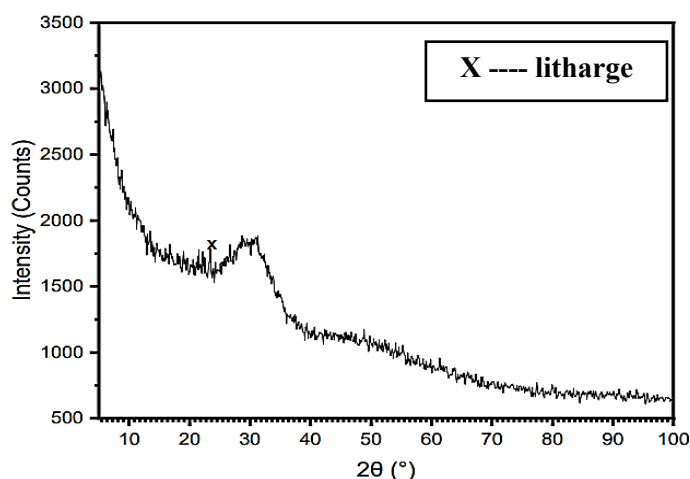


Figure 1 X-Ray Diffraction spectrum of fire assay slags

gangue is required for successful separation. To determine the suitability of gravity separation processes, a concentration criterion (CC) is used. The concentration criterion is shown in equation 1:

$$CC = \frac{Dh - Df}{Dl - Df} \quad (1)$$

Where Dh is the relative density of the heavier mineral, Dl is the relative density of the lighter mineral, and Df is the relative density of the fluid (generally water). Generally, the gravity separation is considered easy when CC is greater than 2.5 (Egbe et al., 2013).

From the XRF analysis results in Table 1 and considering the relative densities of the heavier mineral (Pb = 11.34) and lighter particle (Si = 2.33), a CC value of 7.74 is obtained, indicating that recovery by gravity separation technique is feasible. From Wills and Finch (2016), the percent recovery (% R) is defined by equation 2:

$$\% R = \frac{Cc}{Cf} * x100 \quad (2)$$

Where C = weight /mass of concentrate; F = the weight/mass of feed; c = the grade (assay) of metal or mineral in the concentrate; f = grade of metal/mineral in the feed and t = the grade of metal in tails.

Table 2 Gravity separation results

	Mass (g)	Assay (mg/l)
Feed	500.00	1.66
Concentrate	149.15	4.29

This indicated that about 77% of the lead was recovered from the slag sample using the gravity separation method, which implies that about 23% of the lead could not be recovered.

Froth flotation

Results obtained from Froth Flotation are shown in Table 3. The amount of lead recovered from flotation was calculated by applying the recovery per cent formula (Equation 2). Approximately, 78% of the lead was recovered from the slag sample by the flotation process. The 22% loss could be possibly due to the inefficiency of the process, particle size, pH, retention time and the chemicals (collectors, frothers) amongst other factors, which are likely to have influenced the process.

Table 3 Flotation results

	Mass (g)	Assay (mg/l)
Feed	200.00	1.66
Concentrate	30.51	8.47

Leaching

It has been found that, by comparing different acid extractors at the same concentrations and volume, the chelating characteristics of their anions are possibly the most critical element, more important than the strength of the acid for determining the effectiveness of leaching lead from waste. Ascorbic acid, citric acid, acetic acid, and Ethylenediaminetetraacetic acid (EDTA), all of whose anions are capable of chelating metals (Wadanambi et al., 2008), provided higher percentages of lead recovery than the strongest acid (Nitric acid) at the lowest concentration tested (0.1 mol/L).

Although the oxidizing capability of nitric acid aids in slag dissolution, acetic acid proved to be the most effective

extractor of all the acids tested. The ability of acetate anions to complex cationic metals may explain why acetic acid solutions are more efficient. In consecutive extraction processes applied to environmental matrices, the capacity of acetate to form stable complexes and limit metal re-absorption phenomena has been extensively investigated (Cerceau et al., 2016).

The chemical characterization results for the acid leaching test with acetic acid are presented in Table 4. Equation (3) was employed to determine the percentage recovery by the acid-leaching processing route using the AAS data obtained. The result shows that this processing route was able to recover about 76% of the lead from the slag sample. This implies that about 24% of the lead was lost in the process.

$$\% \text{ Recovery (Pb)} = \frac{\text{concentration of filtrate}}{\text{feed assay}} \times 100\% \quad (3)$$

Table 4 Acid leaching results

	Mass (g)	Assay (mg/l)
Feed	50.00	1.66
Filtrate		1.26

Results from the recovery calculations are presented in Figure 2. From the figure, it is observed that flotation, gravity separation and acid leaching have recovery per cent of 77.83, 77.09 and 75.90 respectively under the same particle size range. Although the application of organic acid (acetic acid) for metal leaching provides a suitable and economic alternative, it still has a low percentage recovery. The flotation process had a recovery percentage slightly higher than that of the gravity separation for recovering lead from fire assay slag. This may be because flotation is a physicochemical process whereas gravity separation is just a physical process (takes advantage of density difference only).

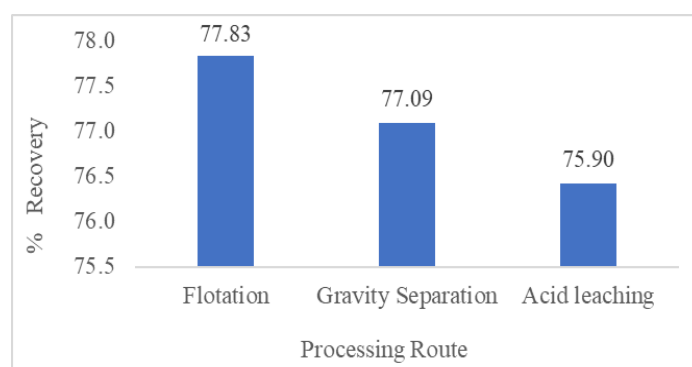


Figure 2 The percent recovery against processing route

Conclusions

The chemical and mineralogical analysis proved the presence of lead as a major element whose concentration in the fire assay slag affects its disposal. Although flotation yielded the highest per cent recovery, gravity separation is the optimum processing approach for lead recovery from fire assay slags when compared to acid leaching and flotation experiments.

This conclusion was reached because the gravity separation experiment took less time to complete. Gravity separation also poses fewer environmental risks, whereas flotation and acid leaching require chemicals that can cause skin irritation and other side effects.

Conflict of Interest Declarations

Authors declare that there is no conflict of interest.

References

- Anderson, C., (2018). Fundamentals of fire assay. <https://doi.org/10.13140/RG.2.2.22438.78408>
- Armah, F.A., Obiri, S., Yawson, D.O., Onumah, E.E., Yengoh, G.T., Afrifa, E.K.A., Odoi, J.O., (2010). Anthropogenic sources and environmentally relevant concentrations of heavy metals in surface water of a mining district in Ghana: a multivariate statistical approach. *Journal of Environmental Science and Health, Part A* 45, pp. 1804–1813. <https://doi.org/10.1080/10934529.2010.513296>
- Asner, G.P., Llactayo, W., Tupayachi, R., Luna, E.R., (2013). Elevated rates of gold mining in the Amazon revealed through high-resolution monitoring. *Proceedings of the National Academy of Sciences* 110, pp. 18454–18459.
- Bazan, V., Brandaleze, E., MarceloValentini, Hidalgo, N., 2015. Characterization of slags produced during gold melting process. *Procedia Materials Science* 8, pp. 851–860. <https://doi.org/10.1016/j.mspro.2015.04.145>
- Cerceau, C.I., Carvalho, C. de F., Rabelo, A.C.S., dos Santos, C.G., Gonçalves, S.M.D., Varejão, E.V.V., 2016. Recovering lead from cupel waste generated in gold analysis by Pb-Fire assay. *Journal of Environmental Management* 183, pp. 771–776. <https://doi.org/10.1016/j.jenvman.2016.08.052>
- Henckens, M.L.C.M., van Ierland, E.C., Driessen, P.P.J., Worrell, E., (2016). Mineral resources: Geological scarcity, market price trends, and future generations. *Resources Policy* 49, pp. 102–111. <https://doi.org/10.1016/j.resourpol.2016.04.012>
- Khaliq, A., Rhamdhani, M.A., Brooks, G., Masood, S., (2014). Metal extraction processes for electronic waste and existing industrial routes: a review and Australian perspective. *Resources* 3, pp. 152–179.
- Michaud, D., (2016). Fire assay procedure. *Mineral Processing & Metallurgy*. <https://www.911metallurgist.com/blog/fire-assay> (accessed 3.29.21).
- Wadanambi, L., Dubey, B., Townsend, T., (2008). The leaching of lead from lead-based paint in landfill environments. *Journal of hazardous materials* 157, pp. 194–200.
- William Andrew Hustrulid, (2006). Fire-assay | chemical process. <https://www.britannica.com/technology/fire-assay> (accessed 3.29.21).
- Wills, B.A., Finch, J.E., (2016). *Wills' mineral processing technology: an introduction to the practical aspects of ore treatment and mineral recovery*, Eighth edition. ed. Elsevier, Amsterdam Boston, Mass Heidelberg.