Research article

Recovering lead from cupel waste generated in gold analysis by Pb-Fire assay

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ABSTRACT

Because of its precision and accuracy, Pb-Fire assay is the most employed method for gold analysis in geological materials. At the second stage of the method, namely cupellation, lead is oxidized to PbO which is absorbed by the cupel, leading to metallic gold as a tiny bend at the bottom of the recipient. After cupellation, cupel becomes highly contaminated with lead, making its disposal a serious risk of environmental contamination. In the present work, a leaching process for removing lead from cupel waste is proposed, which allowed for removing 96% of PbO by weight. After a precipitation step, 92.0% of lead was recovered from leachates in the form of $PbSO_4$. Lead in the solid wastes left by the extraction was above the limit established by Brazilian legislation and these were classified as non-hazardous. Finally, secondary effluents generated after the precipitation step presented lead content more than twenty times lower than that of leachates from cupel waste. Tons of cupel waste are annually generated from gold analysis by Pb-Fire assay. Thus, the proposed method can contribute to prevent the discharge of high amounts of lead into the environment. Also, recovery of lead can help to partially meet the industrial demand for lead compounds.

1. Introduction

Gold has been the most important precious metal throughout the human history. Since the early civilizations this noble metal has been considered a symbol of wealth, power and divinity. Currently, apart from being considered an object of beauty and economic status, gold became a global standard currency, a lead investment and an economic indicator (World Gold Council, 2015).

Gold is found in very low content in the Earth's crust, with an average concentration of 0.005 g t^{-1}. In most of the mining areas, gold content is around 3 g t^{-1}, and those ores presenting 10 g t^{-1} are regarded as having the best quality (Asner et al., 2013; Pitcairn, 2011; Zhang et al., 2015). Because of these very low contents, gold extraction is particularly a high cost process, requiring expensive technologies, energy input, chemicals, and skilled labor. As the more easily accessible gold became scarce, exploration of

deeper, lower grade and remote ore bodies has raised the costs of the operation even more. As a result, there is a lower limit on the grade of the ore from which the gold can be profitably extracted, making the precise quantification of gold in the ores crucial in prospective studies for determining the economic viability of the operation (Fellows, 2010; Shafiee and Topal, 2010).

The lead fire assay (Pb-FA) is the most employed method for the determination of gold in geological material. This method enables a high pre-concentration before analytical quantification and allows for a very precise and accurate determination of gold, with detection limits as low as ng/g (Juvonen and Kontas, 1999; Muir et al., 2005; Vanhaecke et al., 2010). At the first stage of the method, a mixture of ore sample, fluxes (Na_2CO_3, $CaCO_3$, $Na_2B_4O_7$, etc.) and lead oxide (litharge) is smelted in a crucible. The mixture is poured into a mold and allowed to cool, leading to the formation of a mixture of lead (Pb) with all gold (Au) and silver (Ag) present in the ore sample, and a molten slag constituted of the flux and other ore wastes. At the second stage, named cupellation, the metallic lead containing all Au of the sample is placed in an ash-made cupel and heated. This process aims at the removal of Pb as PbO by absorption

of the molten oxide into a porous magnesite cupel by oxidative fusion at 1000–1100 °C, leading to a tiny bed of an Au–Ag amalgam. The amalgam is solubilized by acid digestion and the solution is then used to quantification of Au, which can be carried out by different analytical techniques (Bugbee, 1981; Wall and Chow, 1974).

Only in Brasil, about 1.5 million of Pb-FA analysis is carried out by gold analysis laboratories every year. Roughly, each Pb-FA analysis generates about 90 g of cupel waste, thus resulting in the production and disposal of about 135 tons of waste annually. Because of PbO absorption, cupel waste is heavily contaminated with lead, making its disposal a focus of great concern. Therefore, the development of methodologies for recovering lead from such wastes can contribute to reducing the risk of environmental contamination, as well as to allow for the reuse of Pb, helping to meet the industrial demand for lead compounds.

Recovery of lead from industrial wastes can be achieved through both pirometallurgical and hydrometallurgical processes (Khaliq et al., 2014; Soundarrajan et al., 2012; Zhang, 2013). Pirometallurgical processes usually release SO_x gases and particulate lead to the atmosphere, generating large amounts (up to 25% by weight) of hazardous wastes (Khaliq et al., 2014); therefore an increasing number of reports has focused on the development of more environmentally friendly hydrometallurgical and electrochemical processes for removing lead and other toxic metals from wastes (Ju et al., 2011; Maja et al., 1993; Ruşen et al., 2008). However, to the best of our knowledge, there is no report on the investigation and development of an efficient and reliable methodology for recovering lead from cupel residues.

In the present work, we investigated the application of gravity separation and leaching process, which constitutes two simple and low cost techniques, to extract lead from cupel waste generated from gold analysis by Pb-Fire assay. The two methodologies evaluated The main objective of this study was to convert the hazardous cupel waste into non-hazardous wastes, and recover the lead in the process. The cupel waste were chemically and environmentally characterized, the waste were subjected to gravity separation analysis, and a range of leaching solutions was tested for their efficiency in extracting lead from cupel waste. After selecting the most efficient extraction method, the effluents generated in the process were analyzed to check its hazardousness and the amount of recovered lead was calculated.

2. Materials and methods

All chemicals and reagents were analytical grade and used as received. Ultra pure type II water (conductivity <1.0 mS cm^{-1}) obtained from a Millipore MilliQ water purification system was used in the preparation of all solutions.

2.1. Sampling and milling

Sampling of cupel waste from Pb-FA analysis were carried out in the largest gold analysis laboratory of the State of Minas Gerais, which is the main gold mining State in Brazil. Equivalent amounts of cupel waste, generated over eight months, were collected from randomly selected waste drums using a shovel sampler (Hettipathirana, 2004). A jaw crusher (Rhino e M400) and a pot mill were used for crushing and grinding the waste, respectively. After comminution, samples were homogenized using a Jones splitter and sieved in vertical vibratory sieving system (Viatest) to obtain different granulometric fractions ranging from under 45 μm to 2000 μm.

2.2. Cupel waste characterization

2.2.1. Chemical and mineralogical characterization

For chemical characterization, two pellets containing cupel samples with granulometric size less than 45 μm were prepared. One pellet was prepared in a lithium tetraborate matrix to be used for the determination of light metals and the other was prepared in a potassium pyrosulfate matrix for the determination of heavy metals. Pellets were analyzed in an X-ray fluorescence spectrometer (PHILIPS and PW1480) with a rhodium tube, by varying angles of 2θ, depending on the element to be quantified. Determinations of "loss on ignition" were performed at 1000 °C during 1 h in a muffle furnace, under static air. The same procedure was used for two samples of cupel waste.

For mineralogical characterization, a pellet of the waste in a boric acid matrix was prepared. The mineralogical composition was determined by using a Shimadzu - XRD 6000 spectrometer, coupled with a Fe tube and graphite monochromator with 2θ angles ranging from 10° to 70°.

2.2.2. Classification of the hazards of cupel waste

In order to check their level of hazard, cupel waste were subjected to a leaching test following the procedure established by the Brazilian Norm NBR 10005 (ABNT, 2004a), which is similar to the toxicity characteristic leaching procedure (TCLP) described in EPA method 1311 (US EPA, 2003). The hazard of cupel waste was classified according to the Brazilian Norm NBR10004 (ABNT, 2004b), which establishes classifications for solid wastes of their potential hazards to public health and environment.

Samples of 10.00 g with granulometric size <45 μm were transferred to polyethylene bottles and treated with 200 mL of the extraction solution, prepared by mixing 5.7 mL of glacial acetic acid, 64.3 mL of 1.0 mol.L^{-1} NaOH, and 930 mL of ultrapure water. The bottles were closed and stirred for about 18 h using a rotary shaker Wagner (Marconi e MA160) at room temperature, adjusted to 30 rpm. This process was repeated using 200 mL of ultrapure water instead of the extraction solution, and this sample was used as the analytical blank. Subsequently, the samples were filtered using a 0.45 μm membrane. Extractions were carried out in triplicate and the extracts were subjected to chemical analysis. Arsenic, selenium (hydride generation) and mercury (cold-vapor) were quantified by Atomic Absorption Spectrometry using a Varian AA 275 spectrometer with multi-element hollow cathode lamps. Barium, cadmium, chromium, lead and silver were quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian–Vista-Pro spectrometer, and fluorides were determined by potentiometric analysis using a Orion 710A + potentiometer.

2.3. Enhanced gravity separation analysis

These analyses were carried out to access the possible physical release of lead from cupel waste during comminution. Granulometric fractions of 60–45 μm and <45 μm were subjected to density separation analysis using an INC –L40 Falcon concentrator operated under the conditions of 20% solids by weight, 4.5 L min^{-1} water flow rate, and gravity of 63.89 Hz.

2.4. Chemical extraction of lead

A range of chemicals (e.g. sodium hydroxide, inorganic and organic acids, and their salts) has been shown to efficiently lixiviate lead from wastes, allowing for the recovery of the metal from the leaching solutions.

On the basis of these reports (Aparajith et al., 2010; Cibaa et al., 2003; Ju et al., 2011; Moutsatsou et al., 2006; Niinae et al., 2008;