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.

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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;

Peters, 1999; Raghavan et al., 2000; Wadanambi et al., 2008), a fixed mass of 5.00 g of cupel waste from the fraction 60 μm–45 μm was extracted with 20 mL and 40 mL solutions of different reactants in a range of concentrations as follows: citric acid (0.1, 1.0, and 2.0 mol.L^{-1}), ascorbic acid (0.1, 1.0, and 2.0 mol.L^{-1}), hydrochloric acid (0.1, 1.0 and 2.0 mol.L^{-1}), acetic acid (0.1, 1.0, 2.0, and 8.5 mol.L^{-1}), ethylenediaminetetraacetic acid (EDTA) at 0.1 mol.L^{-1}; nitric acid (0.1, 1.0, 2.0, and 4.0 mol.L^{-1}), urea (200, 350 and 500 g.L^{-1} in 2 mol.L^{-}1 acetic acid) and mixtures of nitric and hydrochloric acid solutions at the following respective concentrations: (0.5 + 0.5), (0.75 + 0.25) and (0.25 + 0.75) mol L^{-1}. Suspensions of solid waste and the corresponding leaching solutions were stirred at 120 rpm for 1 h at room temperature. The mixtures were then filtered through Whatman filter paper Nº 1 and the filtrates were analyzed for lead content by gravimetry. The solid waste left by the most efficient leaching solution was submitted to leaching test (ABNT, 2004a) for environmental classification according to the Brazilian Norm NBR 10004 (ABNT, 2004b), as described in section 2.2.2.

2.5. Precipitation of lead from leachates and environmental classification of the effluent

After selecting the most efficient solution for leaching lead from cupel wastes, the leachates were treated with 0.3 mol.L^{-1} Na$_2$SO$_4$ for the chemical precipitation of lead. The precipitates of PbSO4 were separated by filtration, dried in an oven at 100 °C for 12 h and weighted. This chemical precipitation step led to a secondary effluent, which was analyzed for the inorganic parameters arsenic, lead, and iron, according to the Normative Resolution COPAM/CERH-MG (COPAM/CEH-MG, 2008) for environmental classification of effluents, as described in Section 2.2.2.

3. Results and discussion

3.1. Chemical and mineralogical characterization of cupel waste

The first step in the study was the chemical and mineralogical characterization of the cupel waste. Data from X-ray fluorescence analysis of samples (<0.45 μm) of cupel before and after Pb-Fire Assay (Table 1) clearly show that considerable amounts of PbO are incorporated in the waste upon cupellation. These data were corroborated by mineralogical analysis (Fig. 1), which showed that periclase (MgO), already present in the cupel, massicot and litharge (PbO) are the main crystalline phases in the cupel waste.

Table 1
Chemical composition of cupel before (unused cupel) and after (cupel waste) Pb-Fire Assay.

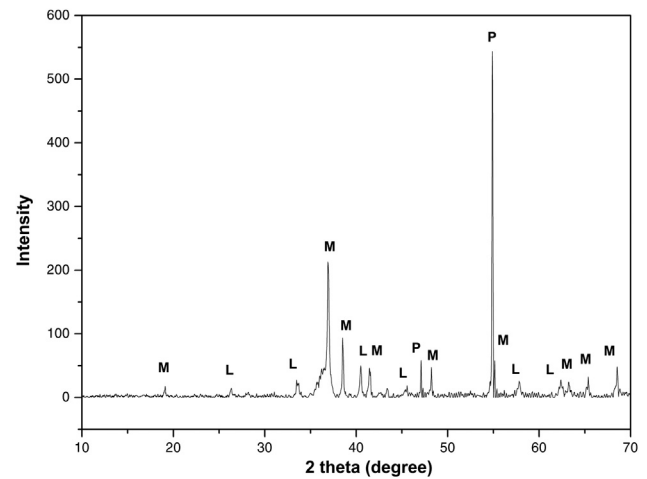| Oxide	Mass (%)		Detection limit
	Unused cupel	Cupel waste	
Al$_2$O$_3$	1.3	0.55	0.1
SiO$_2$	6.5	2.74	0.1
MgO	86	52.80	0.01
Fe$_2$O$_3$	2.9	1.02	0.1
K$_2$O	0.09	0.02	0.01
Na$_2$O	<0.1	0.18	0.1
CaO	4.4	2.61	0.01
PbO	0.05	37.06	0.01
TiO$_2$	0.08	0.03	0.01
Fire losses	–	1.65	–
Total	101.32	98.66	–

Fig. 1. X-ray diffractogram of cupel residue. P, periclase (MgO); M, massicot (PbO); L, litharge (PbO).

3.2. Classification of the hazards of cupel waste

Accessing the level of hazard of solid wastes is crucial for determining and evaluating management strategies for contaminated wastes. According to the Brazilian Norm for hazard classification of solid wastes, these are classified as hazardous (Class I) or non-hazardous (Class II) on the basis of their toxic or infectious properties (ABNT, 2004b). The results from the test (Table 2) showed that the concentration of lead in leachates from cupel waste is more than two thousand higher than the threshold limit established in the Brazilian norm, therefore the cupel waste is classified as hazardous (Class I) waste. These results justify the concern over disposal of cupel waste and highlight the relevance for the development and application of a protocol for removing lead from these wastes.

3.3. Enhanced gravity separation analysis

Both in primary and secondary raw materials, the mineral of interest is commonly heterogeneously distributed in the matrix. Thus, size reduction by crushing and grinding, also called comminution, is necessary for partial liberation and exposure of the target mineral before mechanical or chemical separation.

If comminution of cupel waste resulted in the release of clean PbO particles, it could be possible to remove the mineral by gravity, thus avoiding the consumption of time and chemical in the leaching steps. Gravity separation is a relatively simple and cheap physical process that separates minerals of different densities on the basis of their relative movement in response to gravity and

Table 2
Inorganic parameter concentrations quantified in leachates from cupel waste and maximum limits established by Brazilian Norm ABNT 10004 (ABNT, 2004b).

Parameters	Concentration (mg L^{-1})	Maximum limit (mg L^{-1})
Arsenic	0.62	1.0
Barium	0.13	70.0
Cadmium	0.013	0.5
Lead	**2.065**	**1.0**
Chromium	0.011	5.0
Fluorides	2.6	150.0
Silver	<0.01	5.0
Mercury	<0.0002	0.1
Selenium	<0.01	1.0

resistance to motion offered by a viscous fluid. To an effective separation, there must be a sufficient density difference between the mineral of interest and the gangue. To determine the suitability of gravity separation processes, a concentration criterion (CC) is defined as:

$$CC = \frac{DH - DF}{DL - DF}$$

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).

The main constituents of cupel waste (Table 1) are PbO (massicot and litharge, 37.06 w/w) and (MgO periclase, 52.80 w/w). Taking into account the relative densities of massicot (PbO massicot, 9.64 g cm^{-3}; PbO litharge, 9.35 g cm^{-3}; MgO periclase, 3.58 g cm^{-3}), a CC value ≥ 3.2 is obtained, indicating that, if PbO is released at high degree during comminution, the mineral can be recovered by means of gravity separation process.

To investigate the applicability of gravity separation on lead recovery, a sample of granulometric fraction <0.45 μm was subjected to enhanced gravity separation in a Falcon concentrator and, after separation, lighter and heavier particles were analyzed by X-ray spectroscopy. Fig. 2 compares the diffractograms of the cupel waste, lighter and heavier particles separated in the Falcon concentrator.

Since all samples presented the same chemical constituents, there was no effective release of PbO during comminution of cupel waste. In the gravity separation analyzes, the Falcon concentrator was fed with 2.300 g of cupel waste, 37.06% by weight (about 0.852 g) of which corresponds to PbO (see Table 1). Since the maximum capacity of the concentrator is 100 g, the release of lead would only have been effective if the lighter fraction consisted exclusively of PbO. These results indicated that lead recovery from cupel waste cannot be achieved by gravity separation.

3.4. Chemical extraction of lead from cupel waste

Table 3 shows the wide range of solutions used to extract lead from 5.00 g samples of cupel waste. Except for HCl, increasing the volume of leaching solutions from 20 to 40 mL resulted in higher amounts of extracted PbO, possibly due to faster saturation of the solutions with extracted ions when lower volumes were utilized, thus diminishing the efficiencies of the extraction. Again, with exception of HCl solutions, increasing the concentration of the extracting reagents resulted in higher percentages of PbO recovery. For HCl solutions, it is very possible that precipitation of poorly water soluble PbCl$_2$ was responsible for the low recovery of lead. Thus, the higher the volume or concentration of HCl solutions, the higher the amounts of PbCl$_2$ precipitated and retained during filtration of leachates.

More important than the strength of the acid, the chelating properties of their respective anions is the possible major factor determining the efficiency of leaching lead from the waste, as indicated by comparing different acid extractors, at the same concentrations and volume. At the lowest concentration tested (0.1 mol.L^{-1}), ascorbic acid, citric acid, acetic acid, and EDTA, the anions of which are capable of chelating metals (Wadanambi et al., 2008), provided higher percentages of lead recovery than the strongest acid HNO$_3$. At higher concentrations (1 and 2 mol.L^{-1}), the oxidizing properties of HNO$_3$ play a major role in the dissolution of the waste, but acetic acid remained the most efficient extractor among all tested acids. Again, the higher efficiency of the acetic acid solutions may be due to the ability of acetate anions to complex cationic metals. Indeed, the ability of acetate to form stable complexes and to minimize metal re-absorption phenomena is widely explored in sequential extraction procedures applied to environmental matrices.

The best results were achieved using urea in acetic acid solutions. The most efficient solution for leaching Pb from cupel waste was 500 g.L^{-1} urea in 2 mol.L^{-1} acetic acid, from which 96.03% of
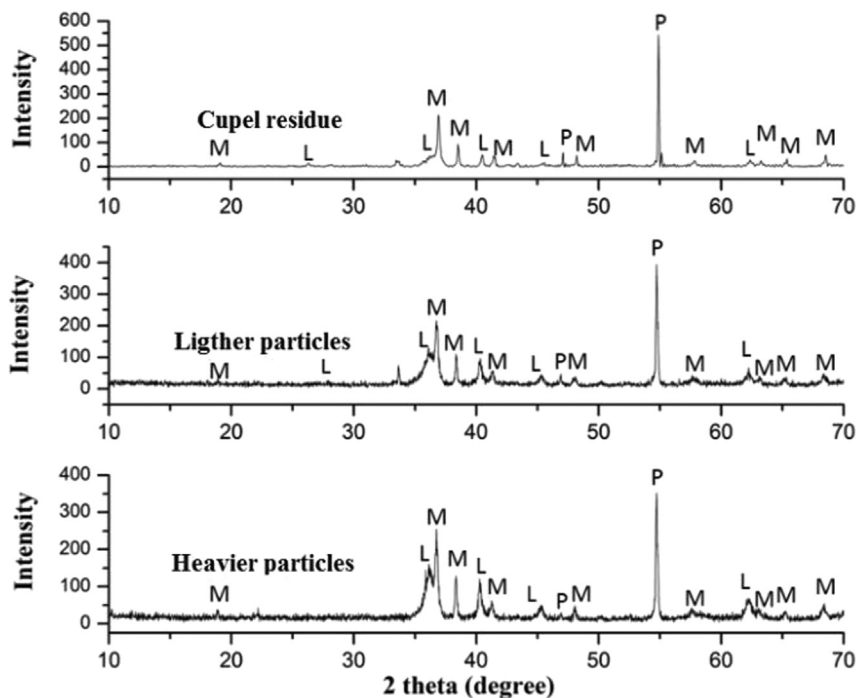

Fig. 2. X-ray diffractograms of cupel residue and of lighter and heavier particles separated by enhanced gravity separation (all in granulometry < 45 μm). P, periclase (MgO); M, massicot (PbO); L, litharge (PbO).

Table 3
Average efficiency of lead extraction by the leaching solutions tested.

Reagent	Concentration (mol L^{-1})	Volume (mL)	% PbO (w/w)
Acetic acid	0.1	20	10.33
		40	12.79
	1.0	20	59.27
		40	69.60
	2.0	20	69.37
		40	70.03
	8.5	20	73.97
		40	81.93
Ascorbic acid	0.1	40	10.77
	1.0		21.55
	2.0		31.75
Citric acid	0.1	20	<0.48
		40	8.35
	1	20	21.37
		40	23.28
	2	20	27.61
		40	37.21
EDTA	0.1	20	9.26
		40	21.20
HCl	0.1	20	2.48
		40	2.49
	1	20	<0.48
		40	2.58
	2	20	<0.48
		40	<0.48
HNO$_3$	0.1	20	0.95
		40	5.72
	1	20	13.90
		40	36.2
	2	20	23.99
		40	40,60
	4	20	34.55
		40	71.99
Acetic acid (with 200 g L^{-1} urea)		40	86.96
Acetic acid (with 350 g L^{-1} urea)	2		88.38
Acetic acid (with 500 g L^{-1} urea)			96.03
HCl + HNO$_3$	0.50 + 0.50	20	<0.48
	0.75 + 0.25		21.46
	0.25 + 0.75		40.33

PbO was solubilized. The reason for such higher efficiency possible relies on the improvement of the acetate concentration as a result of acid-base reaction between urea and acetic acid and on the combination of the complexation abilities of acetate and urea themselves, as well.

After chemical extraction, the remaining solid waste was analyzed for inorganic parameters in accordance with Norm ABNT 10004 (ABNT, 2004b). Table 4 shows that all parameters were below the maximum limit established, classifying the solid waste as non-hazardous (Class II).

Table 4
Inorganic parameters concentration quantified in the leachates from solid wastes obtained after extraction of the cupel waste with 500 mg L^{-1} urea in 2 mol L^{-1} acetic acid.

Parameters	Concentration (mg L^{-1})	Maximum limits (mg L^{-1})[a]
Arsenic	<0.0598	1.0
Barium	0.104	70.0
Cadmium	<0.0165	0.5
Lead	<0.0747	1.0
Chromium	<0.0063	5.0
Mercury	<0.0002	0.1
Selenium	<0.01	1.0

[a] Established by Norm ABNT NBR 10004 (ABNT, 2004b).

Table 5
Inorganic parameter concentration in the effluent generated after chemical precipitation stage.

Parameters	Concentration (mg L^{-1})	Maximum limits (mg L^{-1})*
Arsenic	<0.0598	0.2
Iron	<0.515	15
Lead	**73.0**	**0.1**

*Established by Normative Resolution COPAM/CERH-MG N°1 (COPAM/CERH-MG, 2008).

3.5. Chemical precipitation of lead from leachates

After leaching tests, 20.00 mL of the leachates from extraction of cupel waste with 500 g.L^{-1} urea in 2 mol.L^{-1} acetic acid were treated with 0.3 mol.L^{-1} Na$_2$SO$_4$ in order to precipitate PbSO$_4$. After filtration, the precipitate was dried and weighted, affording 1.11 ± 0.01 g of PbSO$_4$. Considering that cupel waste is composed of 37% PbO by weight (Table 1), and 5.00 g of cupel waste was subjected to the leaching test with 40 mL of extraction solution, the leaching and precipitation steps afforded about 88.3% of total lead recovery in the form of PbSO$_4$. Since each Pb-Fire assay analysis affords around 90 g of cupel waste, about 27 g of Pb can be recovered from the waste of each test, which corresponds to some 300 kg of Pb *per* ton of cupel waste. As previously mentioned, about 135 tons of cupel waste are produced in Brazil every year. Application of the method proposed in the present work could allow for the recovery of 40.5 tons of Pb *per* year, a considerable amount for a country that has no primary production of lead.

3.6. Classification of the secondary effluents obtained after precipitation

The inorganic parameters of the secondary effluent obtained are presented in (Table 5). The results show that the amount of lead in the final effluent, 73.0 mg mL^{-1}, is way above the maximum limit established by Brazilian legislation, preventing these effluents from being directly discharged into water bodies. However, when compared to the lead concentration in the leachates from cupel waste (2.065 mg.L^{-1}, Table 1), these values are important to prove that the method proposed here can result in a substantial reduction on the amount of hazardous wastes produced during gold analysis.

3.7. Economic viability of the process

An economic balance sheet for the lead recovery process from cupel waste is presented in Table 6. Calculations considered the amounts of consumed reagents and recovered PbSO$_4$ from treating 100 kg of cupel waste. The costs related to labor, energy and water consumption and disposal of wastes were not taken into account. These prices refer to analytical grade chemicals and were obtained from one of the largest Brazilian chemical suppliers.

Calculations show that, besides the environmental benefits from generating non-hazard wastes from hazard cupel waste, the

Table 6
Economic balance sheet for treatment of 100 kg of cupel waste.

Consumed reagents	Amount	Price (US$ *per* kg or L)	Total (US$)
Urea	400 kg	5.00	−2000.00
Acetic acid	91.76 L	6.48	−594.60
Sodium sulfate	106.2 kg	16.30	−1731.06
Product			
Lead sulfate	44.4 kg	1142.00	+50,704.80
Balance (US$)			+46,379.14

proposed method represents a profitable procedure for lead recovery in the form PbSO$_4$. The first stage of the Pb-Fire assay consists in smelting a mixture of ore sample, fluxes and litharge (PbO) in a crucible, after which the resulting blend of lead and gold is subjected to the cupellation step. Thus, not only cupel waste, but also the solid crucible waste becomes contaminated with lead.

4. Conclusion

In a previous work (Magalhães et al., 2012), we found that 0.09% of PbO by weight was incorporated into the crucible waste, which was also classified as hazardous, according to the limits established by Norm ABNT NBR 10004 (ABNT, 2004a). After extraction of such waste with hydrochloric and nitric acids followed by chemical precipitation with sodium metasilicate solution, 99.9% (w/w) of lead was recovered, rendering the ultimate waste non-hazardous. Now, we showed that waste from cupellation, presenting a lead content significantly higher than those from crucibles can also be treated in order to successfully recover a substantial amount of lead. By applying the method proposed in the present work, removal of about 96% by weight of lead from cupel waste could be achieved, generating non-hazardous wastes. After a precipitation stage 88.3% of lead was recovered from leachates, in the form of PbSO$_4$. The secondary effluent generated after precipitation, although classified as hazardous, presented a lead concentration about twenty times lower than that of leachates from cupel waste. Together, the methods proposed for treatment of both crucible and cupel waste allowed for recovering almost all lead used in the gold quantification Pb-Fire assay, thus contributing to prevent environmental contamination by lead.

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