



## Rendering wastes obtained from gold analysis by the lead-fusion fire-assay method non-hazardous

Fernanda Batalha Magalhães<sup>a</sup>, Cornélio de Freitas Carvalho<sup>b,\*</sup>, Eduardo Lyse Corrêa Netto Carvalho<sup>b</sup>, Maria Irene Yoshida<sup>c</sup>, Cláudio Gouvêa dos-Santos<sup>b</sup>

<sup>a</sup>SGS GEOSOL Laboratories Ltd., 33200-000 Vespasiano, MG, Brazil

<sup>b</sup>Chemistry Department, Federal University of Ouro Preto (UFOP), Campus Universitário, 35.400-000 Ouro Preto, MG, Brazil

<sup>c</sup>Chemistry Department, Federal University of Minas Gerais (UFMG), Cidade Universitária, 30.123-970 Belo Horizonte, MG, Brazil

### ARTICLE INFO

#### Article history:

Received 5 March 2012

Received in revised form

4 June 2012

Accepted 19 June 2012

Available online 7 July 2012

#### Keywords:

Lead

Crucible waste

Leaching

Chemical precipitation

### ABSTRACT

The classical method of melting lead by fire-assay (Pb-FA) is the most frequently used analytical technique in gold prospecting. The crucible solid waste which is generated in this process is usually characterized by chemical and mineralogical composition, granulometric size distribution, and classified according to Brazilian Environmental Regulations.

This study demonstrates how acid leaching can be used to remove lead from waste originally classified as hazardous by treatment with hydrochloric and nitric acids followed by chemical precipitation in sodium metasilicate solution. It is shown that for every 1000 kg of hazardous waste, 995.6 kg of non-hazardous waste can be recovered.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

The contamination caused by industrial wastes from metallurgical and chemical industries, and the mining of heavy metals typify a serious environmental problem that modern society has been facing for some time. Among wastes containing heavy metals, those containing lead usually attract much concern because of its natural occurrence, its ubiquity in the environment and as a consequence of several industrial activities that favor its wide distribution (Bagchi and Preuss, 2005; Carey and Nagelski, 1996; Göktepe, 2005; Wadanambi et al., 2008). In humans, eventually lead accumulates in bones, but early adverse effects are observed in the central nervous system, plasma, bone marrow and kidneys (Jarosińska et al., 2006; Navas-Acien et al., 2007; Weidenhamer et al., 2010).

In geological materials, lead fusion fire-assay (Pb-FA) (Bugbee, 1981) is the most important chemical analytical method used for the determination of gold. This classical technique involves the preconcentration of the gold and separation into a metallic phase and silicates. It offers high levels of precision and accuracy, with detection limits as low as ng/g (Anderson et al., 2005). These advantages encourage the use of the Pb-FA method to the

determination of the platinum group elements (PGEs): platinum, palladium, rhodium, iridium, ruthenium and osmium (Barefoot and Van Loon, 1999; Rao and Reddi, 2000).

Industrial, research or teaching chemical laboratories using Pb-FA generate crucible waste contaminated with lead from the reduction of lead oxides. In general, this waste is produced after four cycles of fusion, after which the crucible is replaced (Fig. 1), to prevent sample contamination.

Several reports in literature discuss gold analysis by the fire-assay method emphasizing the need to eliminate or reduce the amount of lead-containing waste which is unavoidably produced by this technique (Resano et al., 2006; Balaram, 2008; Berdnikov et al., 2010; Caporali et al., 2010; Roy et al., 2010; Compennolle et al., 2011). According to the Internal Round Robin for Gold Analysis (2007), there are 82 laboratories worldwide using the Pb-FA technique for gold evaluation, all of which will be sources of this waste. In Brazil alone, 1.5 million Pb-FA tests are performed every year, generating about 330 tons of waste containing Pb.

This paper presents a study directed to the environmental characterization and classification of crucible solid waste produced from gold analysis by lead fusion fire-assay. The main objective of this study was to extract lead from waste by a leaching process followed by its chemical precipitation, in order to render such waste less hazardous.

\* Corresponding author. Tel.: +55 31 3559 1711; fax: +55 31 3559 1707.  
E-mail address: [cornelio@iceb.ufop.br](mailto:cornelio@iceb.ufop.br) (C. de Freitas Carvalho).



Fig. 1. Crucible weighing about 0.82 kg, used to contain sample and flow during fusion.

## 2. Materials and methods

### 2.1. Reagents

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

The solution used in the toxicity leaching procedure (TCLP) was prepared by mixing 5.7 mL of glacial acetic acid, 64.3 mL of  $1.0 \text{ mol L}^{-1}$  NaOH, and 930 mL of ultra pure water.

A series of solutions, all of which prepared in ultra pure water with analytical grade chemicals, were used for the extraction steps, namely: sulfuric acid ( $1.79 \text{ mol L}^{-1}$ ), acetic acid ( $1.75 \text{ mol L}^{-1}$ ), hydrochloric acid ( $1.21 \text{ mol L}^{-1}$ ), nitric acid ( $1.43 \text{ mol L}^{-1}$ ), all from MERCK and ascorbic acid ( $0.06 \text{ mol L}^{-1}$ ) from Cinética Química. The following mixtures were also prepared in ultra pure water: glycerol ( $1.00 \text{ mol L}^{-1}$ ), from Merck, and ascorbic acid ( $0.06 \text{ mol L}^{-1}$ ), glycerol ( $1.00 \text{ mol L}^{-1}$ ) and sodium hydroxide ( $3.00 \text{ mol L}^{-1}$ ) from Merck, sodium and potassium tartrate ( $0.53 \text{ mol L}^{-1}$ ), from Sigma–Aldrich, and sodium hydroxide ( $3.00 \text{ mol L}^{-1}$ ). These solutions and their respective concentrations were chosen to accord with those used in previous studies that showed they were efficient in extracting lead (Bonnet et al., 2003; Ferracin et al., 2002; Ioannidis and Zouboulis, 2006; Lee et al., 2003; Moutsatsou et al., 2006; Orhan, 2005; Raghavan et al., 2000).

Stock solutions containing  $1.0 \text{ g L}^{-1}$  of  $\text{SiO}_3$  were prepared by dissolving 2.7874 g  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  (Acros/Fisher) in 1 L of ultra pure water.

### 2.2. Sampling and milling

Sampling of waste from a laboratory that uses Pb-FA for gold analysis was carried out weekly over two months. The process consisted of removing equivalent amounts from randomly selected waste drums, using a shovel sampler (Hettipathirana, 2004). A jaw crusher (Rhino – M400) and a pot mill were used for crushing and grinding the waste, respectively.

After comminution, homogenized samples obtained using a Jones splitter were stored in sealed polyethylene containers.

### 2.3. Waste characterization

#### 2.3.1. Chemical characterization

To characterize the waste chemically, two tablets containing waste sample (diameter less than  $75 \mu\text{m}$ ) were prepared. One tablet was prepared in a lithium tetraborate matrix to be used for the determination of light metals and the other was prepared in a pyrosulfate potassium matrix for the determination of heavy metals. Tablets were analyzed in an X-ray fluorescence spectrometer (PHILIPS – PW1480) with a rhodium tube, by varying angles of  $2\theta$ , depending on the element to be quantified.

Loss on ignition determinations were performed at  $1000 \text{ }^\circ\text{C}$  during 1 h in a muffle furnace under static air.

#### 2.3.2. Mineralogical characterization

A boric acid tablet matrix was used in the characterization of the mineralogy of the waste. A Perkin Elmer GTX-FTIR spectrometer, coupled with a Cu tube with Cu  $K\alpha$  radiation =  $1.54051 \text{ \AA}$  and angles of  $2\theta$  ranging from  $4^\circ$  to  $60^\circ$  was used to determine mineralogical composition.

#### 2.3.3. Granulochemical test

Waste sample (diameter less than  $4000 \mu\text{m}$ ) was homogenized and divided into three fractions of about 100 g for granulochemical tests. Each fraction was sieved through a 2190, 1180, 600, 388 and  $149 \mu\text{m}$  sieve assembly agitated on a Ro-Tap shaker (MARCONI – 750) for 15 min.

The residue on each sieve was pulverized in a pot mill and subjected to lead quantification by atomic absorption spectrometry using an air–acetylene flame (GBC Scientific Equipment – 909 B).

#### 2.3.4. Leaching test

This test was carried out to assess whether the waste is hazardous or not. The procedure established by Norm NBR 10005 (ABNT, 2004a), which is similar to the toxicity characteristic leaching procedure (TCLP) described in EPA method 1311 (US EPA, 2003; Townsend et al., 2008), was followed to obtain leachate extracts. Samples of 50.00 g of waste (grain size  $<9.5 \text{ mm}$ ) were transferred to polyethylene bottles and treated with 1.0 L of the extraction solutions for TCLP, described in Section 2.1.

The bottles were closed and stirred for about 18 h using a rotary Wagner (Marconi – MA160) shaker, at room temperature, with a rotation of 30 rpm. Subsequently, the samples were filtered using a  $0.45 \mu\text{m}$  membrane. This process was repeated using 50.00 mL of ultra pure water instead of the solution and this sample was used as the analytical blank.

The filtrates or leachate extracts were subjected to physical and chemical analysis.

Arsenic, selenium (manual hydride generation) and mercury (cold-vapor) were measured by atomic absorption spectrometry with air–acetylene flame technique using a Varian – AA 275 spectrometer with multi-element hollow cathode lamps. Barium, cadmium, lead, chromium and silver were quantified by optical emission spectrometry with inductively coupled plasma optical emission spectroscopy (ICP-OES) (Varian – Vista-pro) and fluorides were determined by potentiometric analysis (rmo – Orion 710A+).

#### 2.3.5. Solubilization tests

This test must be applied to non-hazardous waste in order to establish it as inert or noninert, i.e., whether or not the parameters after solubilization are below maximum limits of potable water, respectively. The procedure established by Norm NBR 10006 (ABNT, 2004b) was followed for the solubilization test. 25.00 g of waste sample were transferred to a polyethylene bottle and treated with 100.0 mL of ultra pure water. The bottle was closed and stirred for

5 min using a rotary Wagner (Marconi – MA160) shaker, at room temperature, with a rotation of 30 rpm. The bottle was left standing for 7 days and, subsequently, the sample was filtered through a 0.45  $\mu\text{m}$  membrane.

The filtrate was subjected to physical and chemical analysis. This procedure was performed in duplicate and with the analytical blank. Nitrates were determined by spectrophotometric analysis using a FEMTO-700Plus spectrophotometer and chlorides were determined by titration (Clesceri et al., 1998).

#### 2.4. Reduction of Pb concentration in waste

A leaching process employing a number of solutions was used to extract lead from the waste. The effects of concentration and leaching time were investigated for those solutions which presented better leaching results. The resulting solid waste was further submitted to leaching and solubilization steps, as described above (Sections 2.3.4 and 2.3.5).

##### 2.4.1. Chemical extraction method

Three batches of waste residues (diameter less than 4000  $\mu\text{m}$ ) weighing about 80.00 g were transferred to polyethylene bottles containing 300.0 mL of extracting solution.

The bottles were closed and stirred for 1 h using a rotary Wagner (Marconi – 160) shaker, at room temperature, with a rotation of 30 rpm. Afterward, the samples were filtered with a 0.45  $\mu\text{m}$  membrane and washed with 200 mL of ultra pure water.

##### 2.4.2. Concentration effect

To evaluate the effect of acid concentration on lead extraction efficiency, solutions in hydrochloric and nitric acids were tested at 0, 1, 5, 10, 20 and 40% v/v concentrations.

##### 2.4.3. Stirring time effect and secondary waste classification

To evaluate the effect of time on lead extraction efficiency, extract solutions in hydrochloric and nitric acids (5% and 10% v/v) were tested, for  $(2 \pm 0.3)$  h and  $(18 \pm 1)$  h stirring times, to compare test results to the 1-h stirring time.

The secondary waste obtained after chemical extraction was subjected to the leaching and solubilization tests as described in Sections 2.3.4 and 2.3.5 above.

#### 2.5. Treatment of the primary effluent obtained from reduction procedure for Pb concentration

The effluent with high lead content obtained after leaching was submitted to chemical precipitation to remove lead, in order to allow a safe disposal of the effluent.

For treating primary effluents (acid extract) generated in the lead extraction from waste with the nitric acid solution (5% v/v) and hydrochloric acid (5% v/v) steps, a chemical precipitation technique was used.

50.00 mL of the acid extract were treated with the  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  solution (8.00, 50.00 or 150.0 mL). The pH of the mixture was adjusted to 7 (Qualxtron – 8010) under stirring (HOTLAB II – 025) using a 0.1 mol  $\text{L}^{-1}$  solution of NaOH. After neutralization, the mixture was left standing for  $(60 \pm 10)$  seconds.

The addition of 8.00, 50.00 and 150.0 mL of  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  solutions ( $1.0 \text{ g L}^{-1} \text{ SiO}_3$ ) corresponds to  $\text{SiO}_3$  concentrations of 0.16, 1.20 and 3.2  $\text{mg L}^{-1}$ , respectively. The remaining Pb in solution, subjected to chemical precipitation, was quantified by the ICP-OES technique.

This chemical precipitation (CP) step led to a secondary effluent and waste, referred to as CP effluent and CP waste. Inorganic parameters of CP effluents were obtained according to CONAMA

**Table 1**

Chemical composition determined for waste sample using fluorescence X-ray technique.

Oxide	Mass (%)		Detection limit
	Crucible <sup>a</sup>	Waste	
$\text{Al}_2\text{O}_3$	42.4	42.9	0.1
$\text{SiO}_2$	52.2	50.3	0.1
MgO	0.17	0.13	0.01
$\text{Fe}_2\text{O}_3$	2.8	2.0	0.1
$\text{K}_2\text{O}$	1.00	0.86	0.01
$\text{Na}_2\text{O}$	<0.1	1.3	0.1
CaO	0.08	0.09	0.01
PbO	<0.01	0.09	0.01
$\text{TiO}_2$	1.6	2.1	0.01
Loss on ignition	–	0.15	0.01
Sum	99.75	99.92	–

<sup>a</sup> Prior to use.

357 (CONAMA, 2010); CP wastes were characterized by AA technique (GBC Scientific Equipment – 909 B) to quantify lead and were subjected to the leaching test described previously.

### 3. Results and discussion

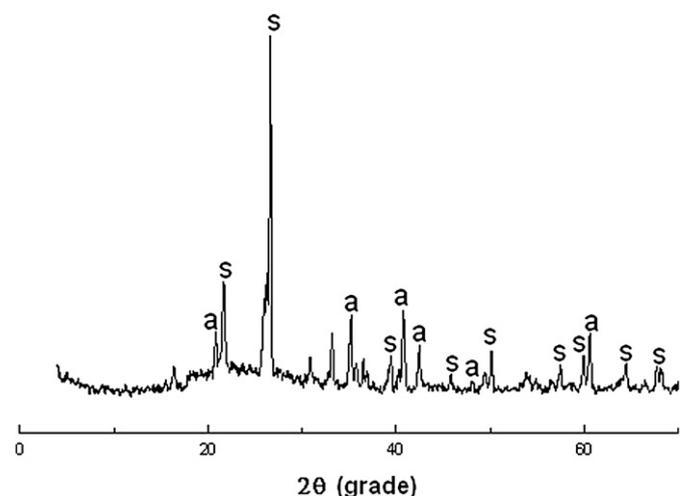
#### 3.1. Waste characterization

Aluminum and silicon oxides are the main components of the crucible. After its use 0.09% of PbO is incorporated in the crucible, while the content of all the other possible oxides did not change significantly (Table 1). Accordingly, the crystalline phase peaks in the X-ray diffractogram of the waste (Fig. 2) are assigned to quartz ( $\text{SiO}_2$ ) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ) (JCPDS-ICCD, 2006). In this diffractogram only those phases with concentrations above 5% w/w are evident.

The presence of lead was detected in all fractions according to the granulochemical tests (Fig. 3). However, fractions with particle sizes below 150  $\mu\text{m}$  had average lead contents above 0.12% w/w, which can be considered to be very high compared to those found in other fractions and in the original sample.

#### 3.2. Waste environmental classification

Environmental classification of solid waste is important for determining strategies for defining supply and management



**Fig. 2.** Waste X-ray diffractogram with quartz ( $\text{SiO}_2 = \text{s}$ ) and aluminum oxide ( $\text{Al}_2\text{O}_3 = \text{a}$ ) peaks identified.

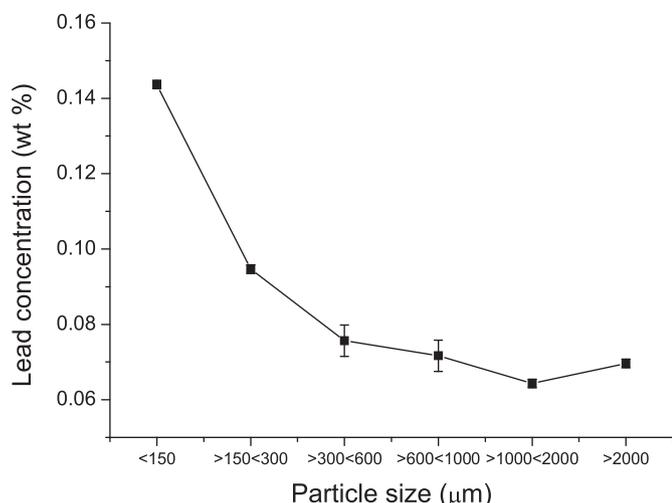


Fig. 3. Lead concentration in fractions of waste with different particle sizes.

systems and the evaluation of treatment effectiveness of the proposed procedures. Norm NBR 10004 (ABNT, 2004c) establishes classifications for solid waste and their potential hazards on the basis of their physical, chemical or infectious properties, which might pose risks to public health and the environment. According to this norm, solid waste can be classified as hazardous (Class I) or non-hazardous (Class II). Class I waste has toxic, flammable, corrosive, reactive or pathogenic properties. A toxic waste is one that when subjected to a leaching test (Section 2.3.5) generates a leachate extract with a contaminant concentration above the maximum established by Annex F of the Norm NBR 10004 (ABNT, 2004c).

If leaching test results do not exceed maximum limits, it is necessary to perform a solubilization test (Section 2.3.5) to further classify waste as inert or non-inert. In this case, waste is subjected to static and dynamic contact with distilled or deionized water, at room temperature, and to a chemical analysis to verify if this waste has constituents which if present in drinking water would be above maximum standards established by Annex G of the Norm NBR 10004 (ABNT, 2004c). If the soluble extract has concentrations above the maximum levels established, the extract is classified as Class II – A – Non-Hazardous – Non-Inert. If all the results are below the limit, the waste is classified as Class II – B – Non-Hazardous – Inert.

Lead concentrations in the extract leachate (Table 2) were found to be above the maximum limit established by Norm ABNT NBR 10004 (ABNT, 2004c), therefore the waste falls under the category “Class I” and it is considered to be hazardous.

Table 2

Inorganic parameter concentrations quantified in samples of leachate extracts obtained for waste and the analytical blank and maximum limits established by Annex F of Norm ABNT NBR 10004.

Parameters	Extract leachate (mg L <sup>-1</sup> )		Maximum limits (mg L <sup>-1</sup> ) <sup>a</sup>
	Waste	Analytical blank	
Arsenics	<0.01	<0.01	1.0
Barium	0.035	<0.005	70.0
Cadmium	<0.001	<0.001	0.5
<b>Lead</b>	<b>26.6</b>	<0.01	<b>1.0</b>
Total chromium	<0.01	<0.01	5.0
Fluoride	<0.10	<0.10	150.0
Mercury	<0.0002	<0.0002	0.1
Silver	<0.01	<0.01	5.0
Selenium	<0.01	<0.01	1.0

<sup>a</sup> Established by Annex F of Norm ABNT NBR 10004 (2004).

### 3.3. Reduction of lead concentration in waste

#### 3.3.1. Chemical extraction

A series of different solutions were scrutinized in order to select the most efficient in extracting lead in the leaching process (Fig. 4). The solution based on sulfuric acid showed only a very low extraction power (less than 5%), which was comparable to that of ultra pure water. A much improved average lead extraction efficiency of around 45% was obtained with the solution of sodium and potassium tartrate. The best results, however, were achieved using the hydrochloric and nitric acid solutions, which extracted lead with an efficiency above 88% (Fig. 4), thereby proving to be the most suitable solutions for the leaching process.

#### 3.3.2. Concentration effects

Once the solutions of hydrochloric and nitric acids were established as the most suitable for extracting lead from crucible wastes, their efficiencies were tested under different concentrations, for 1-h stirring times.

Although the extraction efficiency of hydrochloric acid 5% v/v was much higher than that of the 1% v/v solution, it tended to fall back to an average 70% efficiency at higher acid concentrations (Table 3).

The efficiency of the nitric acid solution peaked at a concentration 10% v/v. Above that concentration, however, the extracting power of the solution was lower than that of the 5% v/v solution.

From the results obtained, both hydrochloric and nitric acid solutions at concentrations 5 and 10% v/v were the most efficient in extracting lead from crucible waste. The effect of stirring time in the efficiency of extraction was also evaluated for these solutions for 1, 2 and 18 h, but the efficiency achieved at 18 h did not differ significantly from those at 1 and 2 h.

#### 3.3.3. Classification of secondary waste

Tables 4 and 5 show extraction parameters for the secondary waste obtained by extraction with hydrochloric and nitric acid solutions 5% v/v.

All of the values listed in Table 4 are below the maximum limits established by Norm ABNT NBR 10004 (ABNT, 2004c), therefore the secondary waste can be classified as Non Hazardous – Class II.

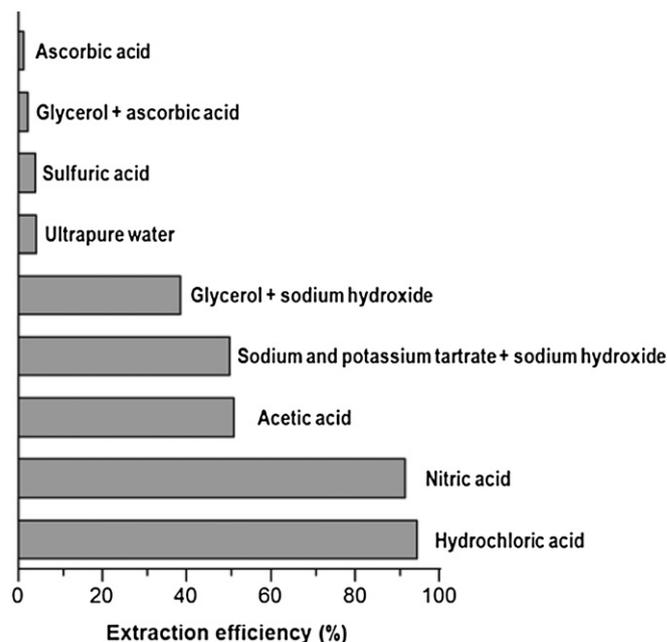


Fig. 4. Average efficiency of lead extraction by a series of solutions. See text for the corresponding concentrations.

**Table 3**

Lead extraction efficiencies by hydrochloric and nitric acid solutions at different concentrations.

Concentration (% v/v)	Extraction efficiency (%)	
	HCl	HNO <sub>3</sub>
0	0.07 ± 0.00	0.17 ± 0.00
1	23.88 ± 0.42	28.69 ± 0.59
5	73.95 ± 0.09	74.06 ± 0.12
10	75.19 ± 0.56	82.55 ± 2.82
20	73.29 ± 1.08	70.94 ± 1.59
40	71.83 ± 0.54	65.03 ± 1.78

Table 5 shows that only the aluminum concentration in the soluble extract was above the maximum limit established by Norm ABNT NBR 10004 (ABNT, 2004c). Thus the secondary waste can be further classified as Non-Hazardous, NonInert or Class II-A.

### 3.4. Treatment of primary effluent

The metals in the effluents generated in the primary stage of lead extraction from waste with nitric acid (5% v/v) and hydrochloric acid (5% v/v) solutions were subjected to chemical precipitation as metasilicates and were characterized for accordance with CONAMA 357 (CONAMA, 2010). Results showed Pb removal efficiency above 99% and there was no change in such efficiency when SiO<sub>3</sub> solutions with 8, 52 and 160 mg L<sup>-1</sup> concentrations were used. In this case, taking costs into account, it is recommended to use the SiO<sub>3</sub> solution with the lower concentration of 8 mg L<sup>-1</sup>.

The primary effluents, generated during chemical extraction, showed iron and lead contents well above the maximum limits established by Norm CONAMA 357 (CONAMA, 2010) (Table 6). After precipitation using sodium metasilicate solution (8 mg L<sup>-1</sup> of SiO<sub>3</sub>), all parameters of the CP effluent fell below the maximum limits established by legislation.

Thus, the CP effluent generated in the chemical extraction whether it be performed using nitric or hydrochloric acid, following chemical precipitation of the metals may legally be released into an industrial wastewater network. However, the release into receiving waters must be preceded by a thorough study of all parameters established by the relevant organizations.

### 3.5. CP waste characterization

AAS characterization of the CP wastes obtained according to procedures described in Section 2.5 indicated lead average concentrations of 1.07% w/w. These wastes from the treatment of primary effluent were classified as Hazardous – Class I, because they had lead concentrations above maximum limits established by

**Table 4**

Inorganic parameters concentration quantified in leachate extracts obtained for secondary waste after treatment with hydrochloric acid (5% v/v) and nitric acid (5% v/v) solutions.

Parameters	Leached extract (mg L <sup>-1</sup> )		Maximum limits <sup>a</sup> (mg L <sup>-1</sup> )
	HCl (5% v/v)	HNO <sub>3</sub> (5% v/v)	
Arsenic	<0.01	<0.01	1.0
Barium	<0.005	<0.005	70.0
Cadmium	<0.001	<0.001	0.5
Lead	<0.01	<0.01	1.0
Total chromium	<0.01	<0.01	5.0
Fluoride	<0.10	<0.10	150.0
Mercury	<0.0002	<0.0002	0.1
Silver	<0.01	<0.01	5.0
Selenium	<0.01	<0.01	1.0

<sup>a</sup> Established by Annex F of Norm ABNT NBR 10004 (2004).

**Table 5**

Inorganic parameters concentration quantified in solubilized extracts obtained for secondary waste after treatment with hydrochloric acid (5% v/v) and nitric acid (5% v/v) solutions.

Parameters	Solubilized extract (mg L <sup>-1</sup> )		Maximum limits <sup>a</sup> (mg L <sup>-1</sup> )
	HCl (5% v/v)	HNO <sub>3</sub> (5% v/v)	
<b>Aluminum</b>	<b>0.71</b>	<b>0.74</b>	<b>0.2</b>
Arsenic	<0.01	<0.01	0.01
Barium	<0.005	<0.005	0.7
Cadmium	<0.001	<0.001	0.005
Lead	<0.01	<0.01	0.01
Chloride	<2.0	1.24	250.0
Copper	<0.01	<0.01	2.0
Total chromium	<0.01	<0.01	0.05
Iron	0.25	0.26	0.3
Manganese	0.04	0.05	0.1
Mercury	<0.0002	<0.0002	0.001
Nitrate (N)	1.46	<0.10	10.0
Silver	<0.01	<0.01	0.05
Selenium	<0.01	<0.01	0.01
Sodium	101.2	41.1	200.0
Zinc	0.18	0.22	5.0

<sup>a</sup> Established by Annex G of Norm ABNT NBR 10004 (2004).

**Table 6**

Characterization of effluents generated before chemical extraction with hydrochloric acid (5% v/v) and nitric acid (5% v/v) solutions (primary effluents) and after chemical precipitation (CP effluents).

Parameters	Total metals (mg L <sup>-1</sup> )				Maximum limits <sup>b</sup> (mg L <sup>-1</sup> )
	Primary effluent (pH = 0.1) <sup>a</sup>		CP effluent (pH = 7.1) <sup>a</sup>		
	HNO <sub>3</sub> (5%v/v)	HCl (5%v/v)	HNO <sub>3</sub> (5%v/v)	HCl (5%v/v)	
<b>Ag</b>	<b>0.79</b>	<b>0.78</b>	0.03	0.02	0.1
B	<0.01	<0.01	<0.01	<0.01	5
Ba	1.72	1.71	0.19	0.03	5
Cd	<0.01	<0.01	<0.01	<0.01	0.2
Cu	0.61	0.48	<0.01	<0.01	1 <sup>c</sup>
<b>Cr</b>	<b>1.4</b>	<b>1.32</b>	<0.01	<0.01	0.5
<b>Fe</b>	<b>119</b>	<b>115</b>	0.02	<0.01	15 <sup>c</sup>
<b>Mn</b>	<b>3.78</b>	<b>3.41</b>	0.41	0.39	1
Ni	0.22	0.19	0.10	0.10	2
<b>Pb</b>	<b>73.3</b>	<b>66.3</b>	<0.01	<0.01	0.5
Sn	<0.1	0.24	<0.01	<0.01	4
Zn	1.22	0.31	<0.01	<0.01	5

<sup>a</sup> Allowable range for discharge: 5–9, according to Norm CONAMA 357 (2005).

<sup>b</sup> Established by Norm CONAMA 357 (2005).

<sup>c</sup> Limits for dissolved metals.

**Table 7**

Inorganic parameters concentration quantified in samples of leachate extracts obtained for CP wastes from treatment of primary effluents generated in chemical extraction.

Inorganic parameters	CP waste leachates (mg L <sup>-1</sup> )		Maximum limits <sup>a</sup> (mg L <sup>-1</sup> )
	HCl (5% v/v)	HNO <sub>3</sub> (5% v/v)	
Arsenic	<0.01	<0.01	1.0
Barium	0.72	0.24	70.0
Cadmium	0.08	0.03	0.5
<b>Lead</b>	<b>33.2</b>	<b>37.5</b>	<b>1.0</b>
Total chromium	0.32	0.40	5.0
Fluoride	<0.10	<0.10	150.0
Mercury	<0.0002	<0.0002	0.1
Silver	<0.01	<0.01	5.0
Selenium	<0.01	<0.01	1.0

<sup>a</sup> Established by Norm ABNT NBR 10004 (2004).

Norm ABNT NBR 10004 (ABNT, 2004c) in extract leachates, according to results shown in Table 7.

Generated CP wastes were more hazardous than the original waste before treatment. However, considering that about 330 tons of wastes containing lead are generated every year in Brazil, if this is submitted to the treatment described here only 1.45 tons will remain hazardous with about 328 tons recovered as non-hazardous.

#### 4. Conclusion

Although silicon and aluminum oxides are the main components of waste, the 0.09% w/w content of its main contaminant, PbO, accounts for its classification as hazardous (Class I).

In this work we presented a simple method for rendering this waste non-hazardous by removing lead through extraction. From both technical and economical viewpoints, the best conditions achieved involve the use of hydrochloric acid and nitric acid extracting solutions at a concentration of 5% (v/v) for a 1-h contact time. From an initial content of 26.6 mg L<sup>-1</sup> in the crucible waste, a reduction to less than 0.01 mg L<sup>-1</sup> lead in the leached extract was accomplished, changing the waste classification from hazardous to non-hazardous. Further steps involving chemical precipitation with SiO<sub>3</sub> solution to remove lead from primary effluents showed an impressive 99.9% efficiency.

Given the nature of the secondary waste and its properties investigated here, it could be used as an alternative source of raw material to similar clay mineral compositions extracted from natural reservoirs. Under severe temperature conditions it should perform well as a lining of heating furnaces, industrial boilers, and for ceramic manufacture. Furthermore it could have a wide range of applications in metallurgical industries (cupola and crucibles) and special industries (glass, mineral furnace calcinations and heat exchangers) (Pukaszewicz, 2001).

All things considered, the reduction in the volume of a Class I – Hazardous passive waste that can be achieved with the methodology described would lead to a significant decrease in management costs and a corresponding reduction in security measures required to prevent environmental contamination by lead.

#### References

- ABNT – Brazilian Association of Technical Standards, 2004a. NBR 10005: Leaching Tests, Rio de Janeiro, 10 pp. (in Portuguese).
- ABNT – Brazilian Association of Technical Standards, 2004b. NBR 10006: Solubilization Tests, Rio de Janeiro, 2 pp. (in Portuguese).
- ABNT – Brazilian Association of Technical Standards, 2004c. NBR 10004: Solid Waste – Classification, Rio de Janeiro, 61 pp. (in Portuguese).
- Anderson, C., Moreno, F., Geurts, F., Wreesmann, C., Ghomshei, M., Meech, J., 2005. A comparative analysis of gold-rich plant material using various analytical methods. *Microchem. J.* 81 (1), 81–85.
- Balaram, V., 2008. Recent advances in the determination of (PGE) in exploration studies – a review. *J. Geol. Soc. India* 72 (5), 661–677.
- Bugbee, E.E., 1981. *A Textbook of Fire Assaying*, third ed. Colorado School of Mines Press, Colorado.
- Bagchi, D., Preuss, H.G., 2005. Effects of acute and chronic oval exposure of lead on blood pressure and bone mineral density in rats. *J. Inorg. Biochem.* 99, 1155–1164.
- Barefoot, R.R., Van Loon, J.C., 1999. Recent advances in the determination of the platinum group elements and gold. *Talanta* 49, 1–14.
- Berdnikov, N., Balaram, V., Cherepanov, A., Avdeev, D., Konovalova, N., Sukharulidze, G., 2010. Some observations on the determination of platinum group elements and gold in black shales. *Res. Commun.* 99 (4), 518–521.
- Bonnet, C., et al., 2003. Alteration of lead silicate glasses due to leaching in heated acid solutions. *J. Non-Cryst. Solids* 323, 214–220.
- Caporali, S., Bellandi, S., Innocenti, M., Lopilato, O., Romualdi, L., Pezzatini, G., 2010. Determination of gold in alloys via potentiometric titration; an alternative to the fire assay. *Gold Bull.* 43 (2), 122–130.
- Carey, M.J., Nagelski, S.D., 1996. Treatment alternatives for lead impacted media: case studies. *Waste Manage.* 16 (4), 263–270.
- Clesceri, L.S., Greenberg, A.E., Eaton, A., 1998. *Standard Methods for Examination of Water and Wastewater*. Sections Nitrate – 4500-NO<sub>3</sub>-E; Chloride 4500-Cl-B, twentieth ed. American Public Health Association (APHA), Washington (CD version).
- Compernelle, S., Wambeke, D., Raedt, I.D., Kimpec, K., Vanhaecke, F., 2011. Direct determination of Pd, Pt and Rh in fire assay lead buttons by laser ablation-ICP-OES: automotive exhaust catalysts as an example. *J. Anal. Atom. Spectrom.* 2 (8), 1679–1684.
- CONAMA, 2010. Conselho Nacional do Meio Ambiente. Resolução NO. 357, de 17 de março de 2005. <http://www.mma.gov.br/port/conama/processos/61AA3835/LivroConama.pdf> (accessed 05.10.10.) (in Portuguese).
- Ferracin, L.C., et al., 2002. Lead recovery from a typical Brazilian sludge of exhausted lead-acid batteries using an electrohydrometallurgical process. *Hydrometallurgy* 65, 137–144.
- Göktepe, F., 2005. Treatment of lead mine waste by a Mozley multi-gravity separator (MGS). *J. Environ. Manage.* 76, 277–281.
- Hettipathirana, T.D., 2004. Simultaneous determination of parts-per-million level Cr, As, Cd and Pb, and major elements in low level contaminated soils using borate fusion and energy dispersive X-ray fluorescence spectrometry with polarized excitation. *Spectrochim. Acta B* 59, 223–229.
- Internal Round Robin for Gold Analysis. Best Performance in 2007, 2007. Laboratory Quality Services International – SGS Minerals Services, 12 pp.
- Ioannidis, A.I., Zouboulis, A.I., 2006. Selective removal of lead and bromide from a hazardous industrial solid waste using limited acid demand and separation factor at ambient conditions. *J. Hazard. Mater.* 131B, 46–58.
- Jarosińska, D., Biesiada, M., Muszyńska-Graca, M., 2006. Environmental burden of disease due to lead in urban children from Silesia, Poland. *Sci. Total Environ.* 367, 71–79.
- Joint Committee of Powder Diffraction Standards, JCPDS-ICCD: PDF-4 Release, 2006. Philadelphia.
- Lee, M.S., Ahn, J.G., Ahn, J.W., 2003. Recovery of copper, tin and lead from the spent nitric etching solutions of printed circuit board and regeneration of the etching solution. *Hydrometallurgy* 70, 23–29.
- Moutsatsou, A., Gregou, M., Matsas, D., 2006. Washing as a remediation technology applicable in soils heavily polluted by mining–metallurgical activities. *Chemosphere* 63, 1632–1640.
- Navas-Acien, A., Guallar, E., Silbergeld, E.K., Rothenberg, S.J., 2007. Lead exposure and cardiovascular disease—a systematic review. *Environ. Health Perspect.* 115, 472–482.
- Orhan, G., 2005. Leaching and cementation of heavy metals from electric arc furnace dust in alkaline medium. *Hydrometallurgy* 78, 236–245.
- Pukaszewicz, A.G.M., 2001. *Tecnologia dos Processos de Fabricação IV – Materiais Cerâmicos*. Coordenação de Mecânica. Centro Federal de Educação Tecnológica do Paraná (in Portuguese).
- Raghavan, R., Mohanan, P.K., Swarnkar, S.R., 2000. Hydrometallurgical processing of lead-bearing materials for the recovery of lead and silver as lead concentrate and lead metal. *Hydrometallurgy* 58, 03–116.
- Rao, C.R.M., Reddi, G.S., 2000. Platinum group metals (PGM): occurrence, use and recent trends in their determination. *Trends Anal. Chem.* 19 (9), 565–586.
- Resano, M., Garcia-Ruiz, E., McIntosh, K.S., Hinrichs, J., Deconinck, I., Vanhaecke, F., 2006. Comparison of the solid sampling techniques laser ablation-ICP-MS, glow discharge-MS and spark-OES for the determination of platinum group metals in Pb buttons obtained by fire assay of platinumiferous ores. *J. Anal. Atom. Spectrom.* 21, 899–909.
- Roy, P., Balaram, V., Sawant, S., Subramanyam, K.S.V., Satyanarayan, M., Vani, K., Srivalli, K., 2010. Determination of platinum group elements and gold in Kimberlites by ICP-MS: modified decomposition procedure using double NiS fire assay followed by Te coprecipitation. *Atom. Spectrosc.* 31 (2), 35–43.
- Townsend, T., Musson, S., Dubey, B., Pearson, B., 2008. Leachability of printed wire boards containing leaded and lead-free solder. *J. Environ. Manage.* 88, 926–931.
- US Environmental Protection Agency, 2003. *Test Methods for Evaluating Solid Waste, SW846*, third ed. Office of Solid Waste and Emergency Response, Washington, DC.
- Wadanambi, L., Dubey, B., Townsend, T., 2008. The leaching of lead from lead-based paint in landfill environments. *J. Hazard. Mater.* 157, 194–200.
- Weidenhamer, J.D., Newman, B.E., Clever, A., 2010. Assessment of leaching potential of highly leaded jewelry. *J. Hazard. Mater.* 177 (1–3), 1150–1152.