Characterization of the lead smelter slag in Santo Amaro, Bahia, Brazil

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ABSTRACT

For 33 years, a primary lead smelter operated in Santo Amaro (Brazil). Since the 1970s, large amounts of Pb and Cd have been widely documented in the blood and hair of people living near the smelter. The plant closed down in 1993, and several years later, the Pb levels in the blood of children under 4 years of age living near the smelter were high, where the disposed lead slag was suspected to be the main source of this contamination. The objective of this study is to elucidate the source of the Pb contamination and any other potentially toxic contamination, focusing on the characterization of the slag. The samples used for this characterization study were taken from the slag heaps. The results of the chemical analysis showed that the major constituents of the slag, in decreasing order of wt%, were the following: Fe_2O_3 (28.10), CaO (23.11), SiO_2 (21.39), ZnO (9.47), MgO (5.44), PbO (4.06), Al_2O_3 (3.56), C (2.26), MnO (1.44), Na_2O (0.27), S (0.37), K_2O (0.26), and TiO_2 (0.25). The Cd content of the slag was 57.3 mg/kg, which is relatively low. The X-ray diffraction and the electron probe microanalyzer X-ray mapping indicated that the major phases in the slag were wüstite, olivine, kirschsteinite, and franklinite. Only spheroidal metallic Pb was found in the slag. The leaching study showed that the slag was stable at a pH greater than 2.8, and only in an extremely acidic environment was the solubilization of the Pb enhanced significantly. The solubilization of Zn was very limited in the acidic and alkaline environments. These results can be explained by the limited leachability of the metallic Pb and Zn-bearing compounds. The leaching study used TCLP, SPLP, and SWEP and indicated that the lead slag was stable in weak acidic environments for short contact times.

1. Introduction

From 1960 to 1993, a primary lead smelter operated in Santo Amaro in the state of Bahia, Brazil that mainly processed a galena (PbS) concentrate from the flotation plant of the Boquira Mine (see Figs. 1a–c and 2a–c). Many studies have indicated that a number of people living near the smelter have been affected by potentially toxic elements, particularly Pb and Cd [1–5]. Epidemiological surveys showed high blood Pb levels in children that lived near the smelter born after the lead smelter closed down [5]. Consequently, a controversy arose regarding the source of this contamination, where the primary suspected source of the toxic elements was the lead blast furnace slag, which had been disposed of near the smelter and was used in roads and houses as construction material. It was thought that the toxic elements from the lead slag were being continuously released into the ground water [5]. This paper presents the characterization of the Santo Amaro lead smelter slag and sheds light on the origin of the Pb and Cd contamination in this region.

Considerable attention has been given to the characterization and stability of both old and new lead slags in France [6–8], the Czech Republic [9,10], Germany [11,12], South Africa [13], Belgium [14], the United Kingdom [15], Namibia, [16], the United States [17], and Canada [18]. It is interesting to note that the stability of the slag depends on the raw material (ore concentrate or solid waste composition) and the process. In various cases, the vegetation and the natural acidity of the soil has partially solubilized the slag matrix, which eventually leads to leaching potentially toxic elements. Despite lead smelting beginning in Brazil at the end of the 1950s, there have been only a few studies on the toxic elements in the slag and their behavior [19].

The Santo Amaro smelter used the following process: classical sinter-roasting, where a Dwight–Lloyd sintering machine was used for the agglomeration; smelting, which used a water-jacket furnace; and refining [20,21]. The smelter could process approximately 46.2×10^3 tons/year of galena concentrate, which consisted of approximately 65% Pb. In the 1970s, the plant produced $14.5–27.7 \times 10^3$ tons/year of Pb and produced 25–40 tons/year of silver [20]. In the roasting-smelting processes, the galena concentrate was blended with limestone made from mollusk shells, scrap iron, coal, and sand [20]. The resulting metal phase was rich in Pb, Ag, Cu, Sb, As, Sn, and Bi, and the slag was rich in Fe, Ca, Zn, and Si

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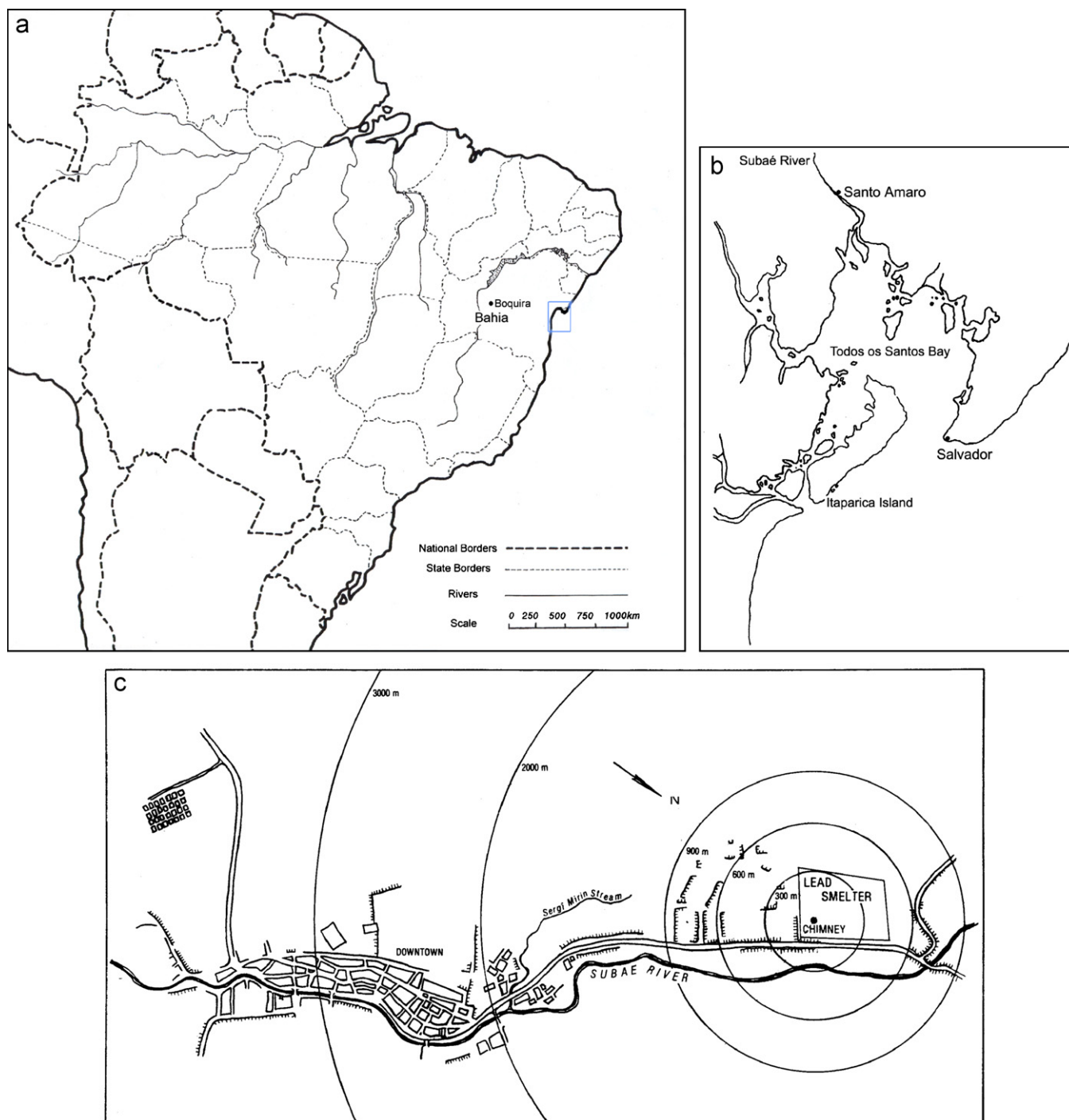
Fig. 1. (a) Map of Brazil showing the location of the state of Bahia and the square in the Todos os Santos Bay. (b) Map of the Todos os Santos Bay, which shows the location of Santo Amaro city and the Subaé River. (c) Map of Santo Amaro city showing the smelter location (adapted from [1]).

[20]. The refining step included "softening" (removing Cu, Sn, Sb, As, and Bi) and desilverization (removing Ag). The Cu solubility in Pb was reduced due to a temperature increase, where the residual Cu was eliminated from the Pb through precipitation as S was added. The Cu-free bullion was then treated to remove Sn, Sb and As through oxidation, where the air temperature was approximately 800 °C. Ag was recovered using the Parkes process, which consisted of adding Zn and precipitating the Ag–Zn intermetallic compounds, which were treated to recover Ag [20,21]. The Bi was also removed as an intermetallic compound by adding Ca and Mg, which were treated to recover a Pb–Bi alloy. Zn was recovered by vacuum distillation at 600 °C. Finally, the residual oxides were eliminated from

the Pb after being washed (leached) in NaOH [20,21]. The slag was tapped off the furnace at a temperature of approximately 1200 °C and was granulated by quenching the molten slag with water [20]. The roast and smelter processes and the raw material, including the galena concentrate, remained essentially the same during the plant operation. However, in its final year, after exhausting the Boquira mine, the plant attempted to operate with a galena concentrate from Peru and Chile.

In the sinter-roasting process, in addition to gases (primarily SO_2 and SO_3), large amounts of flue dust were produced. The total dust production was estimated to be 104–152 kg per tons of the concentrated galena treated, and the average composition of the dust

Fig. 2. (a) Lead smelter chimney stack and the concrete structure of the former plant, as seen from the road. (b) Slag heap showing the re-vegetating heap in the center and a pool that collects the rainwater (to the right of the concrete structure of the former plant). (c) The stack, the re-vegetating heap region, and the road.

was 60% Pb, 10% Zn, 6% Cd, and 5% Fe [20]. Also, the composition could have also included appreciable amounts of As and Sb [21]. The air-pollution control for the roasting and smelter processes at the Santo Amaro smelter consisted of two venturi scrubbers and small chimneys. Until 1976, the liquid effluent was discarded directly into the Subaé river. Afterwards, the slime was precipitated and recycled [20]. In the 1980s, the smelter installed air-pollution control that included filters and a 90 m chimney stack to enhance the SO_2 dispersion.

The goal of this work was to study the chemical composition, mineralogy, and texture of the slag and to evaluate the short-term stability of the potentially toxic elements in the slag in a weak acidic environment.

2. Experimental techniques

2.1. Slag sampling

At the Santo Amaro smelter, 490×10^3 tons of slag heap is estimated to exist, with a volume of approximately $190 \times 10^3 \, m^3$. The particles of the heap are sharp-cornered, brittle and porous. Despite the slag being extremely brittle, the particle sizes of the granulated slag range between approximately 2 and 20 mm.

A sampling campaign was performed in December 2002 at the slag heaps of the Santo Amaro smelter. The vegetation and the impermeable layer of clay soil were removed, and a composite slag sample of roughly 30 kg was collected from the bottom of the heap at different regions, which included slag of different ages.

The slag sample was washed with water to eliminate plant roots, leaves and small particles of soil and clay. After drying at room temperature, the sample was gently homogenized, and smaller samples were collected to be used in the characterization study presented in this work.

2.2. Phase and mineralogical characterization

The X-ray diffraction analysis was performed with a pulverized sample of the lead slag (<37 μm) on a Philips PW1710 diffractometer with Cu K_α radiation at the Department of Mining and Materials Engineering at McGill University (Canada). The interpretation of diffraction patterns was conducted with the assistance of the X'Pert Quantify search match software by PANalytical. From the same department, a scanning electron microscope JEOL 840-A equipped with an X-ray dispersion energy spectrometry system (EDS) was used to evaluate the composition and the texture of the slag particles. The electron probe microanalyzer (EPMA) JEOL 8900L equipped with an X-ray dispersion energy spectrometry system (EDS) and a wavelength-dispersive spectrometer system (WDS) from the Department of Earth and Planetary Science at McGill University (Canada) was used to create a detailed mapping of the major elements of the slag particles. The samples were mounted with an epoxy resin and carefully polished to avoid sample contamination and particle deformation.

2.3. Bulk chemical analyses

Several analytical methods were used to evaluate the slag content to produce representative results. These methods included instrumental neutron activation analyses (INAA), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) applied after near total digestion (with hydrochloric, nitric, perchloric and hydrofluoric acids), and combustion and infrared identifications for total C and S amounts (C/S analyzer by LECO). The total Fe amount was determined by ICP-MS, and Fe^{2+} was determined by titration. For the ICP-MS analysis, the certified standards from the United States Geological Service, Geochemical Exploration Reference Samples (GXR) 1, 2, 4 and 6 were used. For the total C and S analyses, the certified standards from the Mining and Mineral Science Laboratories, Natural Resources Canada, Canadian Standard Reference Materials (CSRM) 1977 and 3144 were used. The neutron activation analyses, with an accuracy of approximately 5%, were performed at the Department of Physical Engineering, University of Montreal (Canada), and the other chemical analyses (including

ICP-MS, ICP-OES, and C/S) were performed at Activation Laboratories Ltd. (Actlabs, Canada), which is a commercial laboratory with the ISO 17025 standard (general requirements for competence of test and calibration laboratories) and the CAN-P-1579 (Canadian Accreditation of Mineral Analysis Testing Laboratories). The density of the slag was measured using the pycnometer method [22].

2.4. Leaching tests

The toxicity characteristic leaching procedure (TCLP) was developed by the United States Environment Protection Agency [23,24] and is useful in identifying the potential hazards of solid waste with a co-disposal assumption. Several metallurgical wastes, including slag, have been classified using this procedure. The main limitation of the conclusions obtained from the TCLP for slag is related to the acid-neutralizing capacity of the specific slag, which lessens over time during the procedure, resulting in amphoteric metals being leached. Therefore, the results are not reliable for long-term stability studies [13]. In the present case, despite the fact that co-disposal of the slag in the landfill and municipal solid waste did not occur, the use of the TCLP test is interesting in that it can simulate the effect of the eventual interaction of the slag with low-molecular-weight organic acids produced by the soil cover over the slag heap. The TCLP experiments used a leaching step where the solid, the size of which was <9.5 mm, was placed in a buffered acetic acid with a pH of 5.0. The solid/liquid ratio was 20, the agitation was 30 ± 2 rpm, the leaching time was 18 ± 2 h, and the temperature was 23 ± 2 °C. After leaching, the liquid phase was separated in a filter size 47 mm or larger [24].

The synthetic precipitation leaching procedure (SPLP), developed by the United States Environment Protection Agency, is more appropriate for mineral processing and metallurgical wastes because it uses a leachant that is intended to simulate the composition of acid rain [13,23–25]. The British Columbia special waste extraction procedure (SWEP) was developed by British Columbia for special wastes, such as metallurgical and mineral wastes [26]. In the SPLP experiments, a leaching step that combines sulfuric and nitric acids is used [13,24,25]. In the SWEP experiments, a leaching step is also used, where the acetic acid is initially at a pH of 5.0 ± 0.2 for 24 h and the solid/liquid ratio is 20 [26].

In the present case, two TCLP tests, one SPLP test and one SWEP test were performed at the Activation Laboratories Ltd. (Actlabs, Canada). The samples sizes were reduced using a mortar and pestle and classified with a 9.5 mm sieve. The potentially toxic content of the solution was analyzed twice by ICP-OES using the certified standards from the United States National Institute of Standards and Technology (NIST) 1643e, SLRS-4 and SLRS-5. Detection limits were set at 0.1 mg/L for Ag, As, B, Ba, Cr, Se and U and 0.01 mg/L for Cd and Hg.

To evaluate the stability of the slag over a wide pH range, samples of the slag whose sizes were smaller than 2.0 mm were placed in a 250 mL Teflon® beaker for about 24 h in a solution of hydrochloric acid (pH 1.1–6.9) and sodium hydroxide (pH 8.2–12.2) at room temperature. The solid/liquid ratio was 10 (20 g:200 mL), and after filtration, the Pb and Zn contents of the liquid phase were analyzed by an atomic absorption spectrophotometer.

3. Results and discussion

3.1. Bulk chemical composition

Table 1 presents the major constituents of the lead slag and the analytical methods. The primary constituents of the slag were Fe, Ca and Si, of which the oxides accounted for 72.6% of the weight. The total slag Fe content was 19.65%, and the Fe^{2+} content was 15.92%;

Table 1
Concentration of the major constituents in the slag.

Element	(wt%)	Method
Fe_2O_3 (total)	28.10	ICP-MS[a]
FeO	20.47	Titration[a]
CaO	23.11	ICP-MS[a]
SiO_2	21.39	INAA[b]
ZnO	9.47	ICP[a]
MgO	5.44	ICP-MS[a]
PbO	4.06	ICP[a]
Al_2O_3	3.56	ICP-MS[a]
C	2.26	C/S[a]
MnO	1.44	INAA[b]
S	0.37	C/S[a]
Na_2O	0.27	ICP-MS[a]
K_2O	0.26	ICP-MS[a]
TiO_2	0.25	INAA[b]
Total	99.98	

[a] Actlabs Job A05-1209.
[b] IGN Job Luizb (December 10, 2004).

therefore, the Fe^{3+} content of the slag was approximately 3.73% (or 5.33% of the Fe_2O_3). In addition, the slag revealed that there was high contents of Zn, Mg, Pb, Al, C, and Mn obtained from the lead pyrometallurgical process, which used limestone, scrap iron, sand and coal to reduce the Pb oxide generated from roasting the galena concentrate. The Zn content was due to the small amount of sphalerite in the galena concentrate and the Zn addition used to recover Ag using the Parkes process [20,21].

Table 2 presents the trace element content of the lead slag and the analytical method used in the analysis. The most common trace elements in the slag were Sr, As, Cu, Cl, Sb, Co, and Ba. It is interesting to note that the Cd content in the slag was only 57.3 mg/kg.

The density of the lead slag was between 3.3 and 3.6 g/cm^3, which is characteristic of the typical density of Pb [21].

Table 2
Trace element contents in the slag.

Element	(mg/kg)	Method
Sr	2470	ICP-MS[a]
As	541	INAA[b]
Cu	538	ICP-MS[a]
Cl	512	INAA[b]
Sb	201	ICP-MS[a]
Co	185	ICP-MS[a]
Ba	169	ICP-MS[a]
Ni	82.2	ICP-MS[a]
Zr	82	ICP-MS[a]
Cr	71.0	INAA[b]
Ce	60.4	ICP-MS[a]
V	58	ICP-MS[a]
Cd	57.3	ICP-MS[a]
U	36.2	ICP-MS[a]
Nd	32.1	ICP-MS[a]
La	29.9	ICP-MS[a]
Mo	28.4	ICP-MS[a]
Sn	23	ICP-MS[a]
Y	21.5	ICP-MS[a]
W	19.8	ICP-MS[a]
Li	15.5	ICP-MS[a]
Th	9.7	ICP-MS[a]
Se	7.7	ICP-MS[a]
In	7.4	ICP-MS[a]
Rb	7.1	ICP-MS[a]
Ag	3.48	ICP-MS[a]
Cs	1.78	ICP-MS[a]
Bi	0.41	ICP-MS[a]
Te	0.4	ICP-MS[a]
Tl	0.18	ICP-MS[a]

[a] Actlabs Job A05-1209.
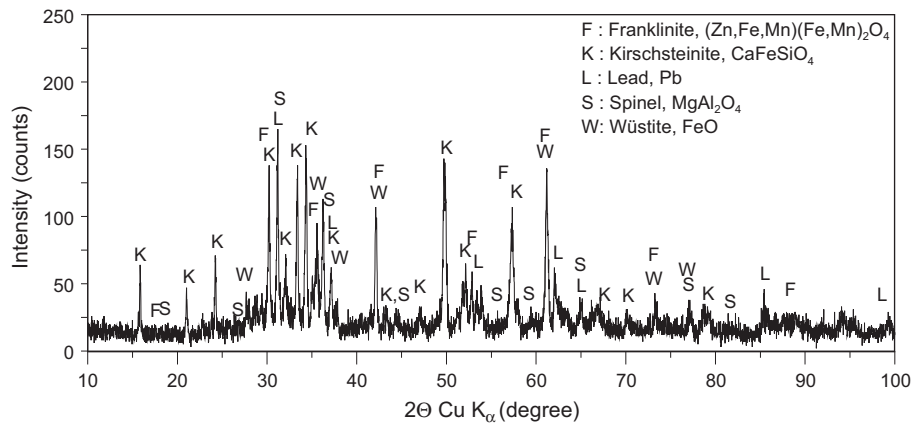[b] IGN Job Luizb (December 10, 2004).

Fig. 3. X-ray diffraction pattern for the lead slag.

3.2. Phase and mineralogical composition

The diffraction pattern of the slag sample is shown in Fig. 3 and reveals a low intensity due to the diffuse scattering caused by the crystallite imperfections, which were formed during the rapid quenching of the slag. This diffraction pattern indicated that the lead slag was mainly composed of kirschsteinite ($CaFe(SiO_4)$), wüstite (FeO), franklinite ((Zn,Fe,Mn)($Fe,Mn)_2O_4$), spinel ($MgAl_2O_4$), and metallic lead (Pb) [6,7,9,10,14,17,18].

Fig. 4a presents a backscattering scanning electron microscope image of the polished slag particles. This image shows several
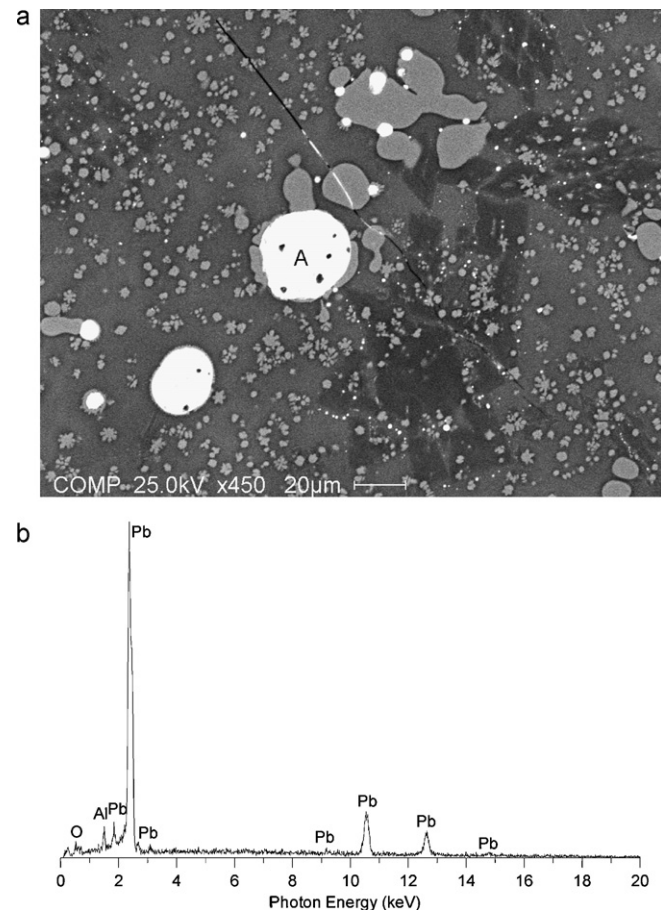
regions with different gray tonalities in the sample. The white spots are metallic Pb (see the EDS spectrum in Fig. 4b), and the light gray regions are fine-grained dendrites. The image shows white spherical metallic Pb spots that range from 1 to 20 μm in size. There are two darker regions in the slag, around the dendrites and the Pb spheroids, which form the slag matrix.

Fig. 4b shows the EDS spectrum of the larger white spots from Fig. 4a. Note that in the EDS spectra, there is a mutual interference of the S $K_{\alpha,\beta}$ and Pb M_α peaks, and it is difficult to determine whether the phase consists of only Pb or both Pb and S. In the present case, however, the S content of the slag was only 0.37%, whereas the Pb content was 4.1%. A significant amount of galena content or lead sulfate was not expected after the roasting and smelting processes.

Fig. 5 shows a backscattering EPMA image of the polished slag particles. Fig. 6a–j shows the EPMA X-ray mapping of the major elements in this slag region. Note that in Fig. 6a, b and c, Pb is not associated with S or O. These results clearly show that Pb in the slag formed into spheroidal particles of metallic Pb [9]. Fig. 6c, d and e shows the association between O, Fe and Zn in the dendrites, which indicates the presence of wüstite (($Fe,Zn)O$) or zincite (($Zn,Fe)O$) as the major phase [7,9,27,28]. Fig. 6c, d, e, h, and j shows the association between Ca, Si, O, and Fe or Zn, which suggests the presence of kirschsteinite ($CaFe(SiO_4)$), olivine (($Ca,Fe)_2SiO_4$), willemite (($Zn,Fe)_2SiO_4$) and melilite ($Ca_2(Fe,Zn)_2Si_2O_7$) as the major phases, as reported by previous EPMA characterization of lead slags [9,27,28].

Fig. 4. (a) Backscattering scanning electron microscope image of a lead slag particle. (b) EDS spectrum of the large white zone, spot A.
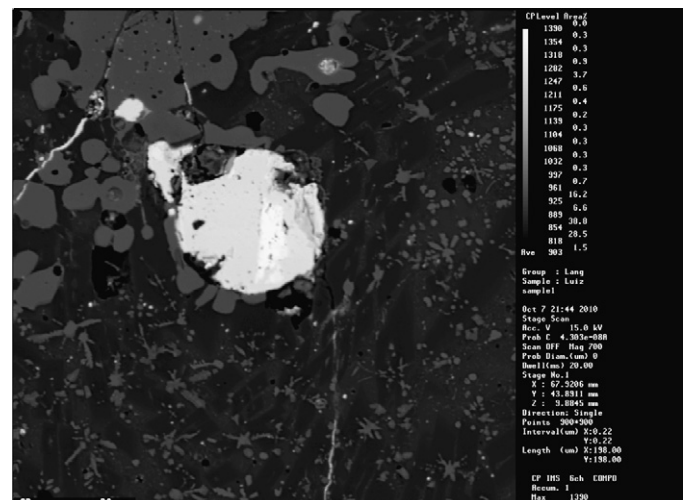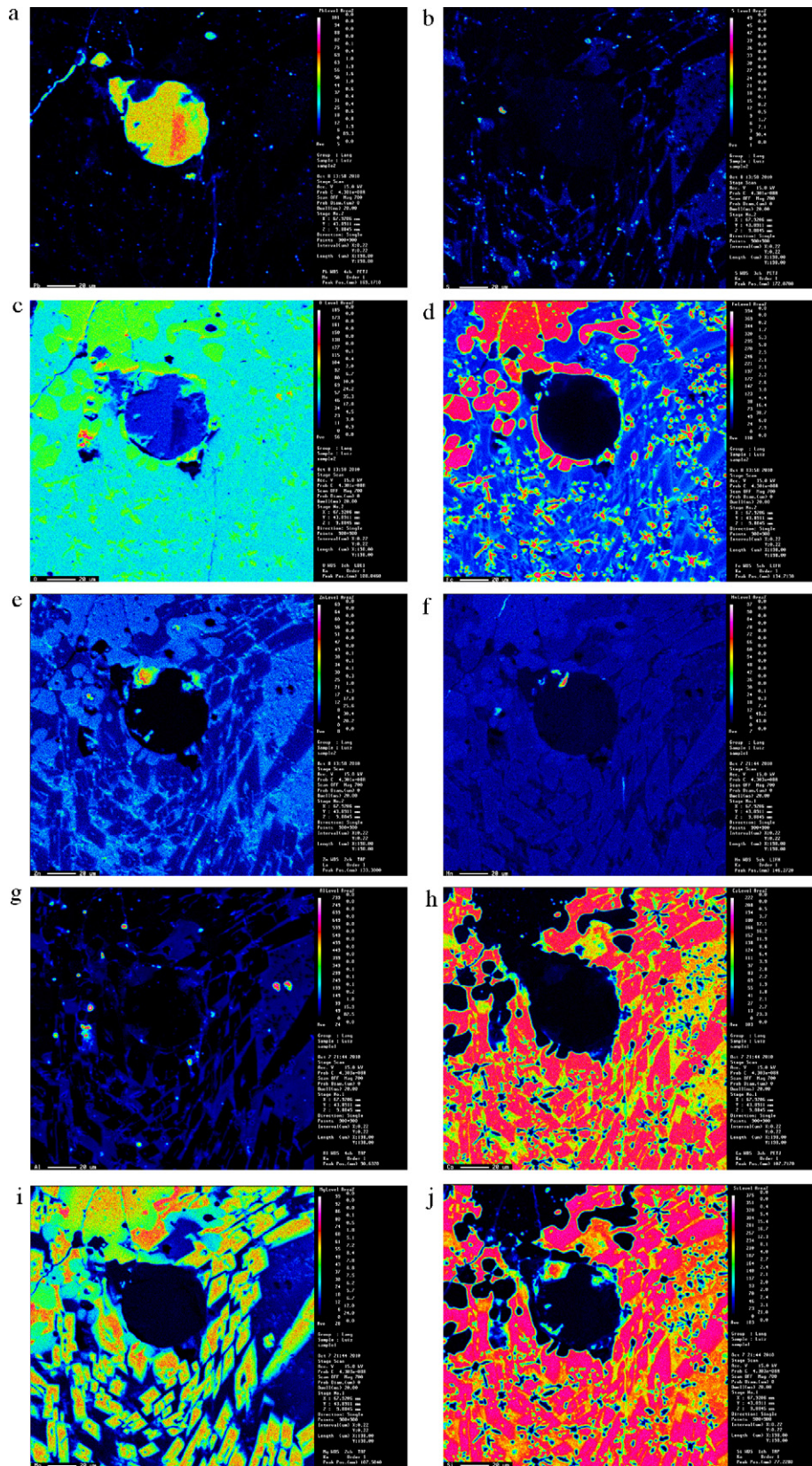
Fig. 5. Backscattering electron probe microanalyzer image of a lead slag particle.

Fig. 6. Electron probe microanalyzer WDS X-ray map of the major elements in the slag for the image shown in Fig. 5: (a) Pb, (b) S, (c) O, (d) Fe, (e) Zn, (f) Mn, (g) Al, (h) Ca, (i) Mg, and (j) Si.
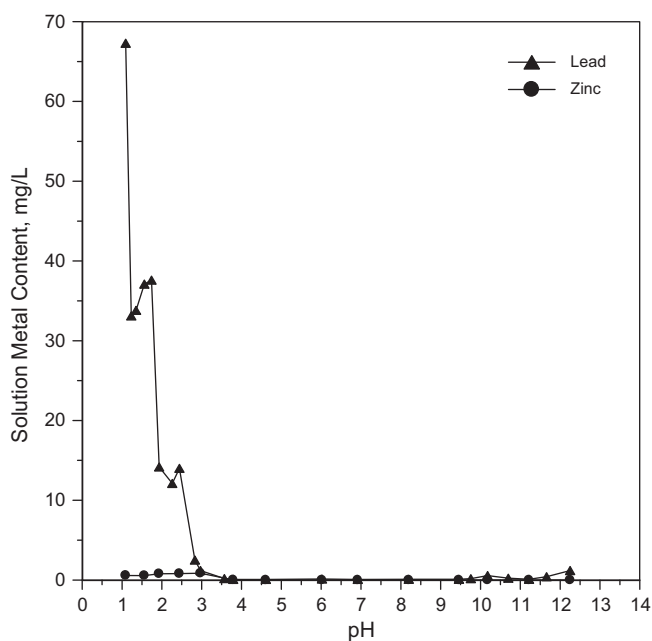
Table 3
Leach analysis (in mg/L).

Element	Ag	As	B	Ba	Cd	Cr	Hg	Pb	Se	U
TCLP 1[a]	nd	nd	0.1	0.3	nd	nd	nd	0.4	nd	nd
TCLP 2[b]	nd	nd	nd	0.3 ± 0.0	0.01	nd	nd	0.85 ± 0.49	nd	nd
SWEP[b]	nd	nd	0.2 ± 0.0	nd	nd	nd	nd	2.05 ± 0.07	nd	nd
SPLP[b]	nd	0.75 ± 0.07	0.25 ± 0.07	nd	0.175 ± 0.007	nd	nd	4.8 ± 0.0	nd	nd
Regulatory Threshold (U.S. EPA) [23,24]	5.0	5.0	–	100	1.0	5.0	0.2	5.0	1.0	–
Regulatory Threshold (Ontario, Canada) [25]	5.0	2.5	500	100	0.5	5.0	0.1	5.0	1.0	10.0

nd, not detected. The detection limit was 0.1 mg/L for Ag, As, B, Ba, Cr, Se, Pb and U and 0.01 mg/L for Cd and Hg.

[a] Actlabs Job A05-1209 g.

[b] Actlabs Job A10-4967. Mean ± standard deviation, for two measures. When the concentration value for a measure was below the detection limit, the mean ± standard deviation is not shown.

Fig. 7. Effect of pH on the leaching of the slag Pb and Zn content.

3.3. Leaching results

The results of the two TCLP tests performed with different samples of the Santo Amaro lead slag are shown in Table 3. The results show that in a weak acidic environment, the solubilization of almost all the elements was below the detection limits. The solution content of the Pb was much smaller (0.4 and 0.85 mg/L) than the acceptable limit of 5.0 ppm [13,23–26]. The SWEP test results confirmed the weak solubilization of the slag Pb content. The solution Pb content was 2.1 mg/L, lower than the acceptable limit. The SPLP test results, despite the leaching solution being stronger, showed a weak solubilization of the slag Pb content. The solution Pb content was 4.8 mg/L, also lower than the acceptable limit.

Fig. 7 shows the Pb and Zn content in the liquid phase in contact with the slag for 24 h over a wide pH range. It shows that the slag was stable when the pH was greater than 2.8 and the solution Pb content was below 5 mg/L. In a more acidic environment, the solubilization of Pb was significantly enhanced (67 mg/L). The solubilization of Zn was limited in the acidic and alkaline environments, where the highest value was approximately 0.84 mg/L at pH a 3.0.

The main environmental implication of the leach test is that the Santo Amaro lead slag is stable, in the short-term, in natural weather. The result is supported by fact that Pb occurred in the slag as metallic particles and the Zn as complex phases, which are stable in most acidic solutions. Cd was not detected in the solution because its content in the slag was only approximately 57 mg/kg. The slag's long-term stability, however, cannot be ensured, and more detailed tests need to be performed to investigate the slag alteration [6–9,16].

4. Conclusions

Discarded, primary lead smelter slag located in Santo Amaro, Brazil was sampled and characterized. The chemical analyses showed that the main constituents of the slag were Fe, Ca, Si, Zn, Mg, Pb, Al, C and Mn. Among the trace elements found most abundantly were Ti, Sr, As, and Cu. The Cd content of the slag was low (57.3 mg/kg). The mineralogical analysis indicated that the slag was primarily composed of wüstite, olivine, kirschsteinite, franklinite, and metallic Pb. The leaching study indicated that the Pb, Zn, Cd and other potentially toxic elements in the lead slag were relatively stable in a weak acidic environment for short contact times, which can be explained by the low leachability of the metallic Pb and the Zn-bearing species and the low content of the Cd.

Acknowledgments

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