ORIGINAL ARTICLE

Evaluation of the chemical stability of a landfilled primary lead smelting slag

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Abstract A primary lead smelter operating in Santo Amaro, Bahia, Brazil, from 1960 to 1993 generated a large amount of slag that was landfilled close to the former smelter and used in roads and houses as a construction material. To evaluate the stability of the slag classical leaching procedures (TCLP, SWEP and SPLP) were applied. In addition, samples of the slag were placed in contact with HCl, HNO₃, HOAc and NaOH solutions for about 24 h at room temperature to simulate acidic and alkaline environments over a wide pH range. In the acidic environment Ca, Fe and Si are strongly solubilized, and Pb and Zn solubilization was significant only below pH 3. The lead slag was also in contact with purified water for a period of 30 days. The results show that Ca and Si were solubilized and Pb, Fe, and Zn were not detected in the solution. The solubilization kinetics are second order processes for both Ca and Si. The initial solubilization rate for Ca and Si are 4.6 and 0.6 mg/L/day, respectively. The main implication of these results is that the major potentially toxic elements of the lead slag landfilled at Santo Amaro were stabilized for a short contact time with pure water and for alkaline and acidic solutions to a pH of about 3 and the groundwater and the surface water contamination found at Santo Amaro smelter region cannot be directly attributed to the landfilled lead slag.

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Introduction

The risk of Pb contamination of surface and groundwater is a permanent concern nowadays especially in regions close to landfill sites. The metals leaching from recent metallurgical slags contain high amounts of potentially toxic elements, such as Pb, As, and Zn, is particularly important to assess the availability and mobility of these elements in the environment (Ettler et al. 2005; Seignez et al. 2008; de Andrade Lima and Bernardez 2010, 2011a, b).

A primary lead smelter which operated at the Santo Amaro city, Bahia, Brazil, from 1960 to 1993 generated a large amount of slag. This smelter used the classical sinter-roasting process followed by smelting and refining (de Andrade Lima and Bernardez 2010, 2011a, b; Habashi 2002). Many studies indicate that people living near this smelter were affected by potentially toxic elements, especially Pb and Cd (Mendes 1977; Loureiro et al. 1983; Tavares et al. 1983, 1989; Carvalho et al. 1984a, b, c, 1985, 1986, 1989a, b, 1995, 1996, 1997, 2003; Silvany-Neto et al. 1985, 1987, 1989, 1996; Tavares and Carvalho 1992). An epidemiological survey of children born after the lead smelter closedown and living near the smelter indicates persistently high blood Pb levels (Carvalho et al. 2003).

Water samples recently collected in a groundwater inspection well located about 300 m from the smelter registered a Pb water content of <0.031 mg/L, a Zn content of <0.013 mg/L, a Cu content of 0.049 mg/L and a Cd content of <0.011 mg/L; however, water samples collected in the smelter protection pool, located close to the landfilled slag showed a Pb content of 0.150 mg/L, a

Zn content of 0.072 mg/L, a Cu content of 0.042 mg/L and a Cd content of 0.001 mg/L. The primary lead slag, disposed close to the smelter and used in road and house building as a construction material, was thought to be the main reservoir of potentially toxic elements continuously releasing them into the surface and groundwater (Carvalho et al. 2003). The slag stability depends on the raw material, the metallurgical process and the environment, and in the cases of slag landfilling, the vegetation and the natural pH of the soil can partially solubilize the slag matrix, and eventually leach potentially toxic elements. This paper addresses the short-term leaching behavior of a primary lead slag, which is useful for evaluating the risk of the lead slag landfilling or stabilization as a construction material and help to clarify the origin of the contamination of potentially toxic elements in the Santo Amaro lead smelter region.

Materials and methods

A sampling campaign was carried out at the slag heaps of the disused smelter. The vegetation and an impermeable layer of clay soil were removed and a total of about 30 kg of slag was collected at the bottom of the heap. The slag sample was washed with water and then with distilled water to eliminate residues from soil and clay. The slag was then dried at room temperature and then in an oven at 60 °C. The dry slag was homogenized and re-sampled.

A scanning electron microscope JEOL 840-A equipped with a X-ray dispersion energy spectrometry system (EDS) was used to evaluate the composition and the texture of the particles of the slag. The samples were mounted with an epoxy resin and carefully polished to avoid sample contamination and particle deformation.

The analytical methods used to characterize the slag included instrumental neutron activation analyses (INAA), induced coupled plasma (ICP-OES) and induced coupled plasma and mass spectroscopy (ICP-MS) with near total digestion (with hydrochloric, nitric, perchloric and hydrofluoric acids), and combustion and infrared identification for total C and S (C/S analyzer). Neutron activation analyses were performed at the University of Montreal (Canada), and the other chemical analyses were performed at Activation Laboratories Ltd. (http://www.actlabs.com).

The toxicity characteristic leaching procedure (TCLP), the synthetic precipitation leaching procedure (SPLP), and the British Columbia special waste extraction procedure (SWEP) were performed at the Activation Laboratories Ltd. and the potentially toxic content of the solution was analyzed twice by ICP-OES (US EPA 1986, 1990; Province of British Columbia 1992; MOE 2000).

To evaluate the stability of the slag over a wide pH range, samples of the slag of sizes smaller than 2.0 mm were placed in a 250 mL Teflon® beaker sealed with parafilm® for 24–29 h in a solution of hydrochloric acid (pH 1.1–6.9), acetic acid (pH 1.0–6.1), nitric acid (pH 1.0–6.0) or sodium hydroxide (pH 8.2–12.2) at room temperature without agitation. The solid/liquid ratio in all tests was 10 (20 g of the slag in 200 mL of liquid). At the end of the leaching test the liquid phase was separated from the slag by decantation. In the case of hydrochloric acid and sodium hydroxide, samples of about 70 mL of the liquid phase were evaporated in an oven at 60–80 °C and the total dissolved solids weight was evaluated with an analytical balance. The total dissolved solids was also used to analyze the metal content using a portable X-ray fluorescence Niton model XL3t 500 by Thermo Fisher Scientific with soil calibration and an excitation time of about 80 s. The contents (Si, Ca, Fe, Pb, Zn) of the solution were analyzed using the sequential ICP-OES Varian model Liberty 150 and element standards from the SpecSol®. For the pH measurements a glass electrode and a Marconi pH Meter (Model MA 522) were used. The pH meter was calibrated using buffer solutions (pH 4 and 7) regularly.

To evaluate the stability of the slag in water, samples of the slag smaller than 2.0 mm were placed in a 250 mL Teflon® beaker sealed with parafilm® for 1–30 days at room temperature without agitation. The solid/liquid ratio in all tests was also 10. At the end of the leaching test the liquid phase was separated from the slag by decantation. The pH was measured before and after contact, and the solution was analyzed by ICP-OES Varian model Liberty 150.

Results and discussion

Table 1 presents the major constituents of the lead slag. These results are in agreement with the lead pyrometallurgical process, which uses limestone, scrap iron, sand, and charcoal to reduce the Pb oxide generated from roasting the galena concentrate (Habashi 2002). The main constituents of the slag are Fe, Ca and Si, of which the oxides account for 72.6 % of the weight. The Pb and Zn slag content are analogous to other lead slags, and the oxides account for 4.1 and 9.5 % of the weight, respectively (Habashi 2002).

Table 2 presents the main trace elements of the lead slag. Worthy of note are the As, Sb, and U slag contents which are relatively high while the Cd slag content is low, which is expected due to the low boiling point of this metal (778 °C) (Habashi 2002).

Figure 1a shows a backscattering scanning electron microscope image of a zone of the polished slag particle.

Table 1 Major elements in the slag

Element	%	Method
Fe_2O_3	28.10	ICP-MS
CaO	23.11	ICP-MS
SiO_2	21.39	INAA
ZnO	9.47	ICP-OAS
MgO	5.44	ICP-MS
PbO	4.06	ICP-OAS
Al_2O_3	3.56	ICP-MS
MnO	1.44	INAA
SrO	0.29	ICP-MS
Na_2O	0.27	ICP-MS
K_2O	0.26	ICP-MS
TiO_2	0.25	INAA
C	2.26	C/S
S	0.37	C/S
Total	100.27	–

Table 2 Trace elements in the slag

Element	mg/kg	Method
Cu	538	ICP-MS
Cl	512	INAA
As	407	ICP-MS
Sb	201	ICP-MS
Co	185	ICP-MS
Ba	169	ICP-MS
Ni	82.2	ICP-MS
Zr	82	ICP-MS
Ce	60.4	ICP-MS
Cd	57.3	ICP-MS
Cr	42.0	ICP-MS
U	36.2	ICP-MS
Th	9.7	ICP-MS
Se	7.7	ICP-MS
Ag	3.48	ICP-MS
Bi	0.41	ICP-MS
Tl	0.18	ICP-MS

Fig. 1 a Backscattering scanning electron microscope image of the lead slag. **b** EDS spectrum of the *white zone*, spot A. **c** EDS spectrum of the *gray zone*, region B

This image shows white spherical spots and dark and light gray zones. Figure 1b shows the EDS spectrum for the larger white particles and this shows that it is metallic lead. Figure 1c shows the EDS spectrum for the slag matrix rich in Ca, Fe, Si, Zn, Mg and Al (de Andrade Lima and Bernardez 2010, 2011a, b).

The results of the TCLP, SWEP, and SPLP tests 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 (US EPA 1986, 1990;
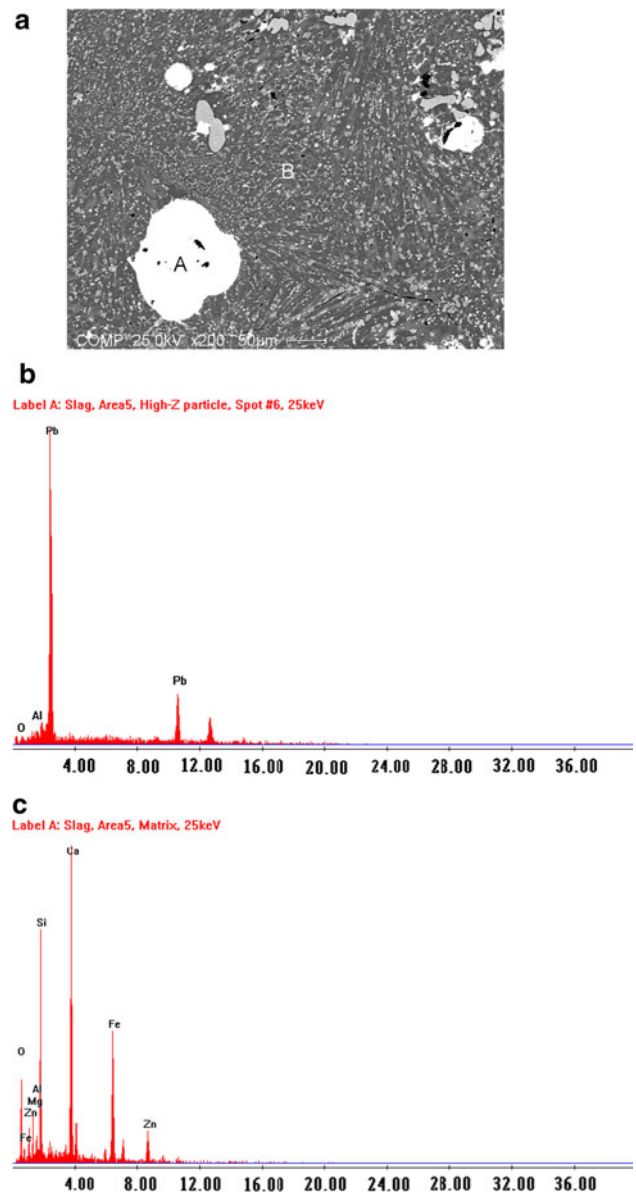
Province of British Columbia 1992; MOE 2000). In the TCLP and SWEP tests the solution contents of all potentially toxic elements, including Pb, As and Cd, were much lower than the acceptable limits. The SPLP test results, despite the leaching solution being stronger, showed a weak solubilization of the slag As, Cd and Pb content; however, all the potentially toxic elements, including Pb, As and Cd, were much lower than the acceptable limit.

Figure 2 shows the solution pH change in the slag leaching tests at 24 h as a function of the initial pH values using HCl or NaOH. There is a remarkable H^+ ion consumption in the region of pH between 4 and 6. It increases

Table 3 Leach analysis (in mg/L)

Element	TCLP	TCLP	SWEP	SPLP	Regulatory threshold (US EPA)
Ag	<0.1	<0.1	<0.1	<0.1	5
As	<0.1	<0.1	<0.1	0.7	5
B	0.1	<0.1	0.2	0.2	–
Ba	0.3	0.3	<0.1	<0.1	100
Cd	<0.01	<0.01	<0.01	0.18	1
Cr	<0.1	<0.1	<0.1	<0.1	5
Hg	<0.01	<0.01	<0.01	<0.01	0.2
Pb	0.4	0.8	2.1	4.8	5
Sb	–	<0.010	<0.010	<0.010	–
Se	<0.1	<0.1	<0.1	<0.1	1
U	<1.0	<1	<1	<1	–
Zn	–	86.7	0.936	302	–

the pH by about 4 units and is probably related to the slag matrix solubilization. Furthermore, at a pH of around 10 there is OH^- consumption which decreases the pH by about 2 Units. It is interesting to note that for pHs 8.2 and 11.22 the contact time was 29 h, but no effects on the final pH were noted for the 5 extra hours of contact.

Figure 3a shows the total dissolved solids in the slag leaching tests at 24 h as a function of the initial pH values using HCl or NaOH. In the acidic region, below pH 3, there is a large amount of dissolved salts indicating poor slag stabilization in this region. In the alkaline region, above pH 10, there is a significant increase in the dissolved salts also indicating poor slag stabilization in this region. Figure 3b shows the metal content of the total dissolved solids in the leaching solution as a function of the initial pH for the acidic environment (pH between 1.1 and 2.4). The resulting

solid has significant amounts of Ca, Fe, Zn, Pb and Mn and the concentration of metals increases exponentially with pH reduction in this case. The Si was not analyzed, however, the solution content is probably significant. It is shown that the Ca and Fe solubilization is higher than the Zn and the Pb solubilization, which indicates that the slag matrix (see Fig. 1) is more susceptible to the acidic environment than the metallic Pb spherical particles.

Figure 4a, b, c, d, e, f shows the Ca, Fe, Si, Zn and Pb solution contents, respectively, after the slag leaching tests for different initial pH values using HCl or NaOH.
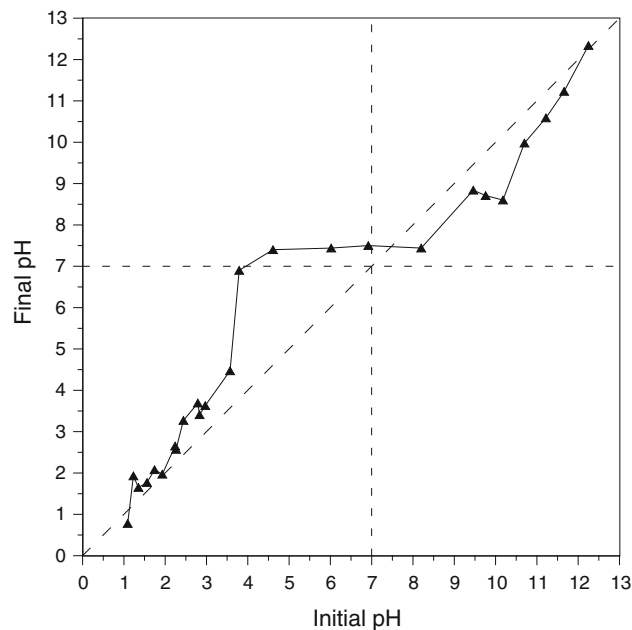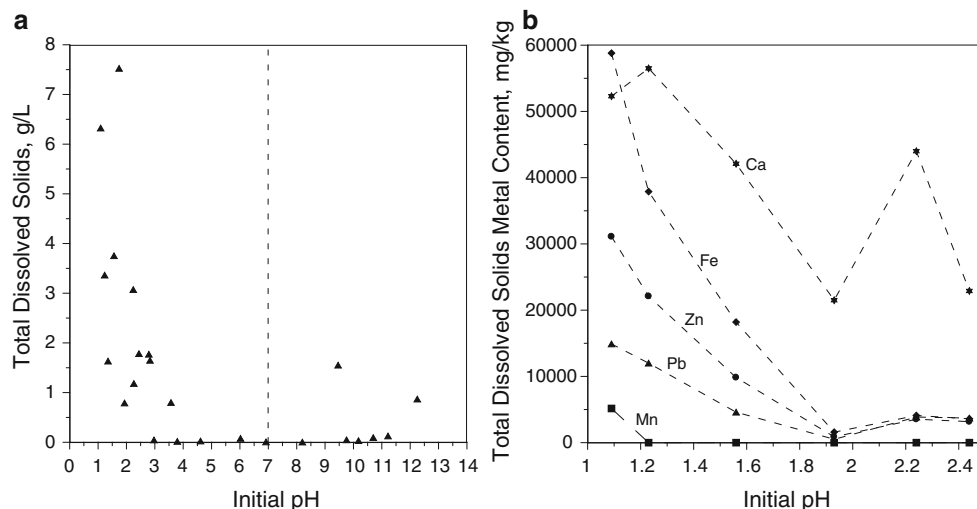

Fig. 2 Slag leaching tests with hydrochloric acids and sodium hydroxide: initial versus final pH values

Fig. 3 Slag leaching tests with hydrochloric acids and sodium hydroxide: **a** total dissolved solids in the leaching solution; **b** metal content of the total dissolved solids in the leaching solution

Fig. 4 Metal solution content after the slag leaching tests with hydrochloric acids and sodium hydroxide: **a** calcium, **b** iron, **c** silicon, **d** zinc, **e** lead
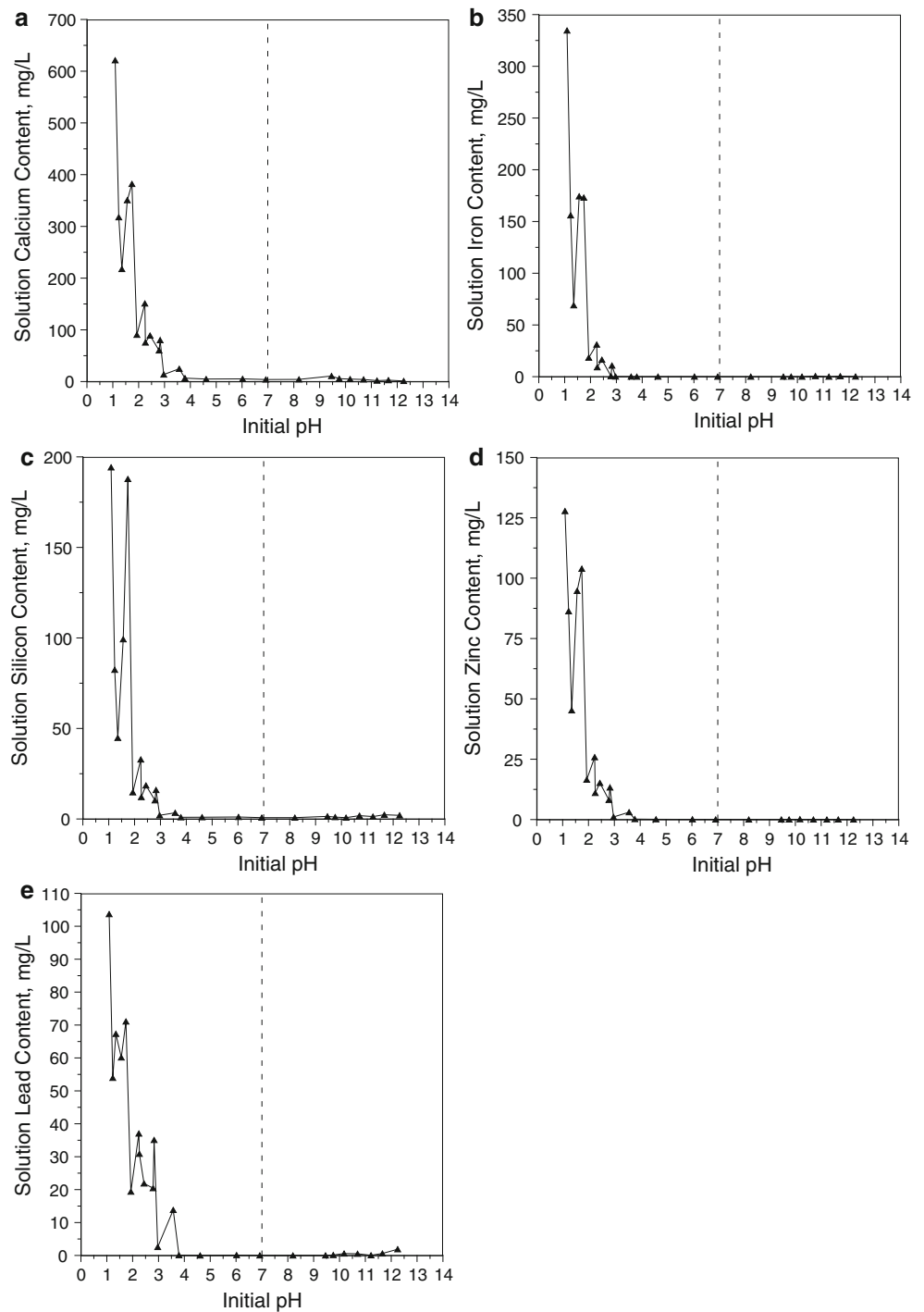
It shows that the slag is not easily leachable when the pH is greater than 3. In a very acidic environment, however, the solubilization of the elements was significantly enhanced.

Figure 5 contrasts the solution pH change in the slag leaching tests as a function of the initial pH values for nitric acid (HNO_3) and acetic acid (HOAc). It is interesting to note that the H^+ ion consumption in the region of pH between 4 and 6 is high for the three acids. The hydrochloric (see Fig. 2) and nitric acids present low H^+ ion consumption in the region of low pH, and the acetic acid presents a high consumption at low pH values, due to the complexing capacity and the slag matrix solubilization.

Figure 6a, b shows the solution content elements after the slag leaching tests for different initial pH values using nitric acid and acetic acid. It shows that the slag is stable at pH > 3 for HNO_3 and for HOAc the slag is stable at pH > 4. The elements of the slag matrix have an analogous behavior to the lead. All elements are solubilized in very
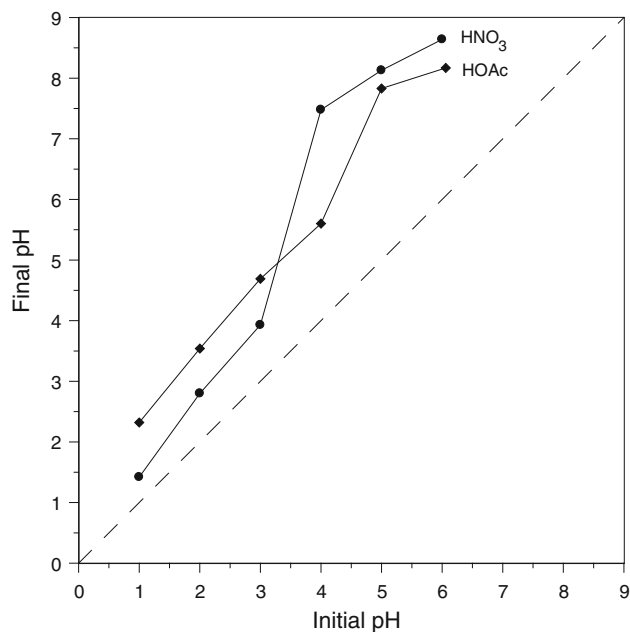
Fig. 5 Slag leaching tests with acetic and nitric acids: initial versus final pH values

acidic solution. The acetic acid strongly leaches the iron at low pH; however, below pH 3 a precipitation of a brownish-red amorphous powder can be seen, probably the coordination compound iron (III) acetate, which has low solubility in water and adsorbs the solubilized elements. It explains the reduction in the metals in the solution at low pH with HOAc.

Figure 7a shows the solution pH–time evolution due to the water–slag interaction. It can be observed that low water acidity is enough to cause an effect on the water–slag interaction, and the difference between the initial and the final pH increases initially and decreases with time indicating activity on the slag surface. Figure 7b shows the Ca, Si, Fe, Zn and Pb solution content time evolution due to the water–slag interaction. Only Ca and Si demonstrate

significant solubilization by water for a contact time of 30 days.

The batch reactors used in this study have a constant volume; therefore, the global kinetic models for Ca and Si solubilization can be given by pseudo-homogeneous kinetics as follows:

$$\frac{dC(t)}{dt} = k\left[C_f - C(t)\right]^\alpha \tag{1}$$

$$C(0) = 0 \tag{2}$$

where, C is the element solution content, t is time, k is the kinetic constant, C_f is the final element solution content, and α is the reaction order. In this study Eq. 1 was numerically integrated using the initial condition given by Eq. 2 and the fourth order Runge–Kutta method. The kinetic parameters (k, α, C_f) were evaluated by curve-fitting using the nonlinear least square criteria and an optimization method.

The fitted kinetic model for the Ca and Si water solubilization are given by:

$$\frac{dC_{Ca}(t)}{dt} = 1.24 \times 10^{-2}(16.7 - C_{Ca}(t))^{2.1} \text{ mg/L/day} \tag{3}$$

$$\frac{dC_{Si}(t)}{dt} = 4.62 \times 10^{-2}(3.41 - C_{Si}(t))^{2.1} \text{ mg/L/day} \tag{4}$$

Figure 7b shows the experimental results and the results of the kinetic model. As can be seen in Eqs. 3 and 4, the reaction order (α) in the case of Ca and Si are almost two and the initial solubilization rate for Ca and Si are, respectively, 4.6 and 0.6 mg/L/day.

The main environmental implication of the leaching tests is that the major potentially toxic elements in the primary lead smelter slag from Santo Amaro (Pb and Zn) are relatively stable for short contact time with pure water and for alkaline and acidic solutions to a pH of about 3. This result is supported by fact that Pb occurs in the slag as metallic particles and the Zn in complex oxides and

Fig. 6 Element solution content after the slag leaching tests with: **a** nitric acid, **b** acetic acid
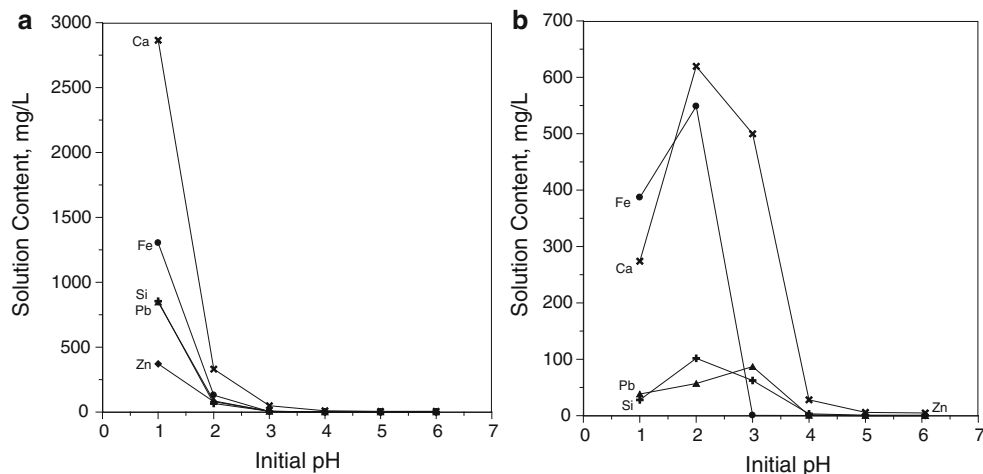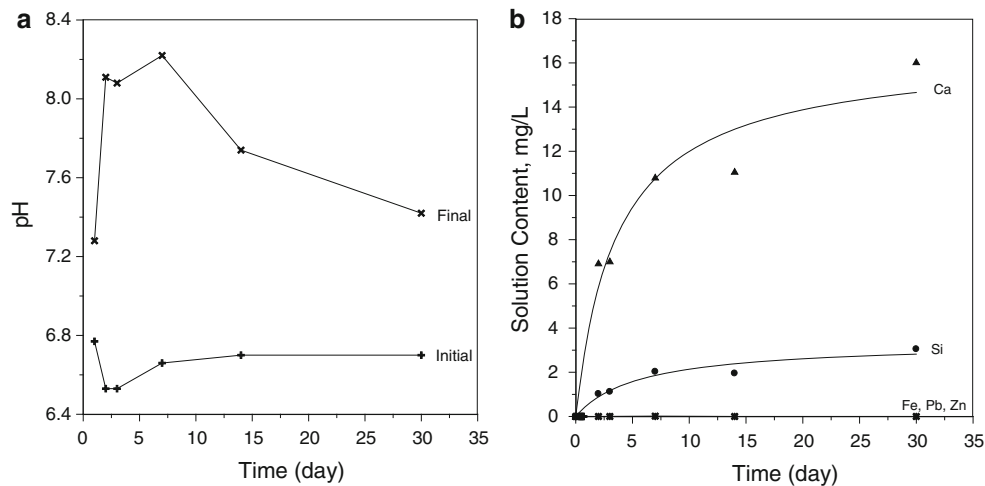
Fig. 7 Time evolution of the solution content due to water–slag interaction: **a** initial and final pH. **b** Ca, Si, Fe, Pb, and Zn solution content

silicates (de Andrade Lima and Bernardez 2011b), which are stable in most acidic solutions. Therefore, the surface water and the groundwater contamination found in the region of the Santo Amaro smelter cannot be directly attributed to the landfilled lead slag.

Conclusions

Discarded primary lead smelter slag was sampled and characterized. The short-term leaching behavior of this slag was investigated using contact times of about 24 h with HCl, HNO_3, HOAc and NaOH in solutions with pH between 1.1 and 12.2. The slag alteration was observed in the acidic (below pH 3.0) and in the alkaline (above pH 10.0) environments. In the acidic environment Ca, Si and Fe from the slag matrix were strongly solubilized. The Pb and Zn solubilization was significant only in a very acidic environment (below pH 3). The lead slag was also put in contact with purified water for a period of 30 days. The results show that Ca and Si were solubilized and Pb, Fe, and Zn were not detected in the solution. The implication of the leaching tests is to assert that, for short-term contact, the potentially toxic elements of the primary lead smelter slag of Santo Amaro is stable in a large range of pH (3–10). Therefore, the surface water and the groundwater contamination found in the Santo Amaro smelter region cannot be directly attributed to the landfilled lead slag. In this context, slag remobilization or chemical processing is not a viable solution to reduce the heavy metal contamination in the region of the former smelter.

References

Carvalho FM, Silvany-Neto AM, Lima MEC, Mendes JLB, Quaglia GMC, Tavares TM (1984a) Poluição por cádmio e lesão renal em habitantes de Santo Amaro da Purificação. Bahia. Revista Baiana de Saúde Publica 11:116–122 (in Portuguese)

Carvalho FM, Waldron HA, Tavares TM, Barreto ML, Silvany-Neto AM (1984b) Multiple causes of anaemia amongst children living near a lead smelter in Brazil. Sc Total Environ 35:71–84

Carvalho FM, Tavares TM, Souza SP, Linhares P (1984c) Lead and cadmium concentrations in the hair of fishermen from the Subaé River Basin, Brazil. Environ Res 33:300–306

Carvalho FM, Silvany-Neto AM, Lima MEC, Tavares TM, Waldron HA (1985) Lead poisoning among children from Santo Amaro, Brazil. Bull Pan Am Health Organ 19:165–175

Carvalho FM, Silvany-Neto AM, Lima MEC, Tavares TM, Alt HF (1986) Cadmium concentrations in blood of children living near a lead smelter in Brazil. Environ Res 40:437–449

Carvalho FM, Silvany-Neto AM, Melo AMC, Chaves MEC, Brandão AM, Tavares TM (1989a) Cadmium in hair of children living near a lead smelter in Brazil. Sci Total Environ 84:119–128

Carvalho FM, Silvany-Neto AM, Lima MEC, Melo AMC, Galvão AL, Tavares TM (1989b) Chumbo e cádmio em cabelos de crianças de Santo Amaro da Purificação. Bahia. Ciência e Cultura 41:646–651 (in Portuguese)

Carvalho FM, Silvany-Neto AM, Barbosa AC, Cotrim CRL, Tavares TM (1995) Erythrocyte protoporphyrin versus blood lead: relationship with iron status among children exposed to gross environmental pollution. Environ Res 71:11–51

Carvalho FM, Silvany-Neto AM, Peres MFT, Gonçalves HR, Guimarães GC, Amorim CJB, Silva JAS Jr (1996) Intoxicação pelo chumbo: zincoprotoporfirina no sangue de crianças de Santo Amaro da Purificação e de Salvador. Ba. Jornal de Pediatria 72:295–298 (in Portuguese)

Carvalho FM, Silvany-Neto AM, Peres MFT, Gonçalves HR, Guimarães GC, Amorim CJB, Silva JAS Jr (1997) Chumbo no sangue de crianças e passivo ambiental de uma fundicao de

chumbo no Brasil. Jornal de Pediatria 73:S11–S14 (in Portuguese)

Carvalho FM, Silvany Neto AM, Tavares TM, Costa ACA, d'El Rei Chaves C, Nascimento LD, de Andrade Reis M (2003) Blood lead levels in children and environmental legacy of a lead foundry in Brazil. Revista Panamericana de Saude Publica 13:19–23 (in Portuguese)

de Andrade Lima LRP, Bernardez LA (2010) Characterization of the heavy metals contamination due to a lead smelting in Bahia, Brazil. In: Siegmund A, Centomo L, Geenen C, Piret N, Richards G, Stephens R (eds) Lead-Zinc 2010. TMS (The Minerals, Metals & Materials Society), pp 917–927

de Andrade Lima LRP, Bernardez LA (2011a) Characterization of the lead smelter slag in Santo Amaro, Bahia, Brazil. J Hazard Mater 189:692–699

de Andrade Lima LRP, Bernardez LA (2011b) Isotope source signatures for a primary lead smelter located close to Todos os Santos Bay, Brazil. Soil Sediment Contam 20:672–687

Ettler V, Jehlička J, Mašek V, Hruška J (2005) The leaching behaviour of lead metallurgical slag in high-molecular-weight (HMW) organic solutions. Mineral Mag 69:737–747

Habashi F (2002) Textbook of pyrometallurgy. Métallurgie Extractive Québec, Canada

Loureiro S, Spinola AG, Carvalho FM, Barreto ML (1983) Lead poisoning and hookworm infection as multiple factors in anaemia. Trans R Soc Trop Med Hyg 77:321–322

Mendes R (1977) Effects of lead on workers living in areas with highly endemic intestinal helminthiasis. J Occup Med 19:498–499

MOE (2000) Ministry of the Environment Regulation 558/00, Environment protection act, Schedule 4. Leachate quality criteria, Ontario

Province of British Columbia (1992) Waste Management Act: Special Waste Regulation Schedule 4, Parts 1 and 2. Queen's Printer, Victoria, pp 72–79

Seignez N, Gauthier A, Bulteel D, Buatier M, Damidot D, Potdevin JL (2008) Leaching of lead metallurgical slag and pollutant mobility far from equilibrium conditions. Appl Geochem 23:3699–3711

Silvany-Neto AM, Carvalho FM, Lima MEC, Tavares TM (1985) Determinação social da intoxicação por chumbo em crianças de Santo Amaro-Bahia. Ciência e Cultura 37:1614–1626 (in Portuguese)

Silvany-Neto AM, Carvalho FM, Lima MEC, Tavares TM, Azaro MGA, Quaglia GMC (1987) Chumbo e cádmio no sangue e estado nutricional de crianças de Santo Amaro Bahia. Revista de Saúde Pública 21:44–50 (in Portuguese)

Silvany-Neto AM, Carvalho FM, Chaves MEC, Brandão AM, Tavares TM (1989) Repeated surveillance of lead poisoning among children. Sci Total Environ 78:179–186

Silvany-Neto AM, Carvalho FM, Tavares TM, Guimarães GC, Amorim CJB, Peres MFT (1996) Lead poisoning among children from Santo Amaro, Bahia, Brazil in 1980, 1985, and 1992. Bull Pan Am Health Organ 30:51–62

Tavares TM, Carvalho FM (1992) Avaliação da exposição de populações humanas a metais pesados no ambiente: exemplos do recôncavo baiano. Quim Nova 15:147–154 (in Portuguese)

Tavares TM, Carvalho FM, Souza SP, Linhares P (1983) Absorção e intoxicação pr chumbo e cádmio em pescadores da região do Rio Subaé. Ciência e Cultura 35:360–366 (in Portuguese)

Tavares TM, Brandão AM, Chaves MEC, Silvany-Neto AM, Carvalho FM (1989) Lead in hair of children exposed to gross environmental pollution. Int J Environ Anal Chem 36:221–230

U.S. EPA (1986) Toxicity characteristic leaching procedure, Appendix 1, Federal Register, 51(216)

U.S. EPA (1990) Characteristics of EP Toxicity. Paragraph 261.24, Federal Register, 45(98)