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Vol. 13(19), pp. 1973-1978, 7 May, 2014
DOI: 10.5897/AJB2013.13276
Article Number: 8934BFC44521
ISSN 1684-5315

http://www.academicjournals.org/AJB

African Journal of Biotechnology

Full Length Research Paper

Chemical characterization and local dispersion of slag generated by a lead recovery plant in Central Mexico

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Received 13 September, 2013; Accepted 3 April, 2014

A toxic waste "slag" generated in a lead (Pb) recovery plant was characterized and its local "slag" dispersion was monitored. The major constituents of the "slag", in increasing weight percent, were CaO (1.5), PbO (3.4), SiO_2 (5.2), Na_2O (17.8), SO_3 (27.5) and Fe_2O_3 (40.7). The "slag" was alkaline with a pH of 10 and an electrical conductivity of 606 dS m^{-1}. Tests for Pb leaching indicated that, in a moderately acid environment, as much as 8 mg Pb L^{-1} may be washed out of the "slag"; there are amounts that are well above the limits set by Mexican legislation. The highest concentration of Pb in soil surrounding the recycling plant (447 mg Pb kg^{-1}) was found 50 m southwest of the recovery plant. Due to its high Pb level and easy dispersion into the environment, the health of human settlements in the area could be at risk.

Key words: Toxic waste, alkaline material, Pb leaching.

INTRODUCTION

According to Mexican Official Norm (NOM-052-SEMARNAT-2005), exhausted lead-acid automobile batteries are considered hazardous wastes, due to their high lead (Pb) content. In Mexico, 95% of the acid batteries discarded are recycled, and the efficiency of Pb recovery is about 98% according to the Instituto Nacional de Ecología (INE, 2000). A typical process for recycling Pb from acid batteries includes their rupture, draining of the acid, separation of the components containing Pb and its recovery by smelting (Faé et al., 2011). During the smelting process, a solid material called "slag" is generated. It contains a high concentration of Pb, among other toxic elements (Coya et al., 2000; Penpolcharoen, 2005).

"Slag" and the fumes from the chimneys of the smelting furnace thus represent a risk to human health and the environment (Andrade Lima and Bernardez, 2011). Pb causes a wide range of biochemical, physiological and behavioral dysfunctions. The mechanisms of Pb toxicity to living organisms at the molecular level are caused by covalent binding to proteins, oxidative damage and interference with divalent cation specific sites, such as

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Table 1. Components of the Pb“slag” determined by X-ray fluorescence.

Compound	Weight (%)
TiO_2	0.056
P_2O_5	0.084
V_2O_5	0.104
ZnO	0.110
K_2O	0.121
CrO_3	0.142
Sb_2O_3	0.158
MgO	0.195
As_2O_3	0.246
MnO	0.255
CuO	0.278
Cl	0.317
Al_2O_3	0.423
BaO	0.554
SnO_2	0.890
CaO	1.460
PbO	3.430
SiO_2	5.180
Na_2O	17.840
SO_3	27.450
Fe_2O_3	40.740

those recognized by Ca^{++} (Quintanar-Escorza et al., 2007). It also causes damage to DNA (Yáñez et al., 2003). In addition, high Pb levels in the atmosphere generate a negative impact on human health, plants, animals and microorganisms (Akmal et al., 2005; Zhuang et al., 2009). As a result of excessive intake of Pb by plants and animals this element can reach the food chain, which becomes a potential risk to human health (Zhuang et al., 2009).

Farago et al. (1999) reported Pb levels that ranged between 792 to 39 mg Pb kg^{-1}in top soils (0-5 cm) at distances of 0.5 and 3.5 km, respectively, from a Pb recycling plant in southern Sweden. In fact, in a study conducted in north Mexico, it was found that, in human populations located at 5 and 0.9 km from a smelter, the average Pb level in blood (ABL) was 7.8 and 21.8 µg dL^{-1}, respectively (García et al., 1999). Regarding to the Pb recovery plant under study, which generates 1500-2000 t of “slag” yr^{-1}, previous reports indicated that workers present a high Pb ABL of 74.4 ± 21.9 µg dL^{-1}(Quintanar-Escorza et al., 2007).

The objectives of this study were to chemically characterize the industrial “slag” generated by a Pb recovery plant and to monitor the local dispersion of “slag” in the plant surroundings soils.

MATERIALS AND METHODS

The study site was a Pb recovery plant located in the State of Guanajuato, Mexico at 101º 41' 00"west, 21º 07' 22" north and an altitude of 1798 m. The smelter is dedicated to the recovering of Pb from exhausted automotive and industrial batteries. Ten samples of approximately 1 kg each were taken from the “slag” heaps of the Pb-recovery plant. Sampling was conducted at different points of the deposit; samples were homogenized and a representative subsample of 1 kg was taken for further analysis.

Several analytical methods were used to evaluate the chemical composition of the “slag”, including wavelength dispersive X-ray fluorescence spectrometry (WDXRF) and energy dispersive spectrometry coupled to scanning electron microscopy (SEM-EDS) (JEOL JSM model 5910LV-27, JEOL Ltd.1-2, Musashino 3-chome, Akishima, Tokyo 196-8558, Japan). These methods were used to examine the microstructure and the elemental composition of the “slag”. Both types of analyses were performed on pulverized (0.8 mm) samples of “slag”. The detection limit for elements using the SEM-EDS method is 0.25 weight percent (wt%) and for this reason SEM-EDS was complemented by inductively coupled plasma atomic emission spectrometry (ICP-AES) for the analyses of toxic metals present at concentrations lower than 0.25%. Three samples of “slag”, each of 1 g, were digested with hydrochloric, nitric, perchloric and hydrofluoric acids (Andrade Lima and Bernardez, 2011).

The methods used here to determine the toxicity of hazardous wastes were developed by the Environmental Protection Agency of the United States of America (USEPA). They include the Toxicity Characteristic Leaching Procedure (TCLP) which was employed to determine the mobility of the metals in the “slag”. Extraction tests were carried out by mixing 10 g of “slag” with acetate buffer at a ratio of 1:20 w/v (pH 4.95 ± 0.05). After stirring for 18 h at 30 ± 2 rpm at a temperature of 25 ± 2°C (Andrade Lima and Bernardez, 2011) and the Synthetic Test Precipitation Leaching Procedure (SPLP) was applied to simulate the extraction of solutes leached out by acid rain. Another extraction test was performed by exposing 10 g of “slag” to a weak solution of nitric acid/sulfuric acid (pH 5 ± 0.1) at a ratio of 1:20 w/v. Again, stirring was maintained for 18 h at 30 ± 2 rpm at a temperature of 25 ± 2°C (Andrade Lima and Bernardez, 2011). Extraction using $Ca(NO_3)_2$ to determine available Pb was also performed (Tao et al., 2006). Soluble anions (carbonates, CO_3^{-2}; bicarbonates, HCO_3^- and sulfates, SO_4^{-2}) were determined in the extract using the AS-20 method. Electrical conductivity (EC) and pH of the “slag” were determined by AS-18 and AS-02 methods, respectively (NOM-021-SEMARNAT-2000).

Samples of soil (0-30 cm depth) were collected at 14 different locations (north, south, east, west, south-west and north-west) at distances ranging from 50 to 300 m away from the recycling plant. Soil samples were air dried and stored in polyethylene bags until analysis. The pH was determined in an aqueous solution by the AS-02 method, while the EC was determined according to the AS-18 procedure. The organic matter content (OM) was analyzed by the AS-07 method, soil texture by the method AS-09 using the Bouyoucos procedure and the cation exchange capacity (CEC) by the method AS-12. All established methods are described in NOM-021-SEMARNAT-2000. Soil concentrations of Ca, Fe, Na and Pb were determined following the ICP-AES protocol. The distribution of Pb around the recycling plant was represented by an iso-curve map constructed using the program Surfer version 10.

RESULTS AND DISCUSSION

The major compounds found in “slag” were: CaO, PbO, SiO_2, Na_2O, SO_3 and Fe_2O_3, at wt% of 1.5, 3.4, 5.2, 17.8, 27.5 and 40.7, respectively (Table 1); similar values have been reported in other studies (Penpolcharoen, 2005; Andrade Lima and Bernardez, 2011). Table 2 summarizes the elemental analysis carried out by SEM-EDS and ICP-AES. The main elements in the metal fraction corresponded to 23.3, 12.6, 3.4%, Fe, Na and Pb, respectively; similar proportions were reported by Faé et al. (2011). Fe and Na are contained in the $NaHCO_3$, Fe filings and mineral coal that are added to the molten during the melting

Table 2. Elemental composition of the Pb "slag".

Element	Weight (%)
Al	0.38 ± 0.15[a]
As	0.52 ± 0.11[a]
C	7.19 ± 0.69[a]
Ca	1.57 ± 0.06[a]
Fe	23.28 ± 0.43[a]
Na	12.56 ± 0.38[a]
O	37.19 ± 0.40[a]
Pb	3.36 ± 0.29[a]
S	10.80 ± 0.16[a]
Si	2.78 ± 0.05[a]
Cd	0.04 ± 0.02[b]
Co	0.01 ± 0.01[b]
Ni	0.02 ± 0.03[b]

[a]SEM-EDS and [b]ICP-AES methods.

process (Penpolcharoen, 2005; Faé et al., 2011). The high O content (37.2%) suggests that a large proportion of these metals are present as oxides (Penpolcharoen, 2005; Andrade Lima and Bernardez, 2011).The concentration of Pb in the "slag" was 29 and 51 times higher than the maximum values allowed by Mexican legislation for agricultural soils and industrial zones, which are 400 and 700 mg kg^{-1}, respectively (NOM-147-SEMARNAT/SSA1-2004).The "slag" also contains the toxic trace elements As,Cd, Co and Ni, as shown by SEM-EDS and ICP-AES (Table 2). Only As was above the limits allowed by the Mexican legislation (NOM-147-SEMARNAT/SSA1-2004). In a study conducted in the municipality of Villa de la Paz, San Luis Potosi, Mexico levels of Pb and As in surface soil were 400 and 100 mg kg^{-1}, respectively. Here, the infant population suffers severe DNA damage due to high levels of these elements in the body (Yáñez et al., 2003). However, the levels of Pb and As in the "slag" are higher than those reported in this study, which highlights the danger posed to the population that is exposed to this pollutant.

Microscopic observation shows that the "slag" resembles a newly bituminized road surface containing prominent black grains amongst a mass of otherwise mostly homogenous material (Figure 1a). A special feature of the "slag" is the so called "white zones" that, continuing with the above analogy with a macadamized surface, resemble quartz grains. When enlarged, it is apparent that these "bright spots" possess defined structures (Figure 1b). An EDS spectrum of a "white zone"* (Figure 1b) showed high signal intensities for Fe, Pb, S, Ca, Na, O, C and As but low signals for Si and Al (Figure 1c). High signal intensities correspond to elevated concentrations of elements with large atomic numbers and, thus, the lighter areas represent elevated levels of Pb and other metals with high electron densities. The EDS spectra taken by Andrade Lima and Bernardez (2011) of larger "white spots" of "slag" indicated similar compositions to those found here.

In aqueous solution, the "slag" is alkaline, with a high EC, containing large concentrations of CO_3^{-2-}but relatively low amounts of HCO_3^- and SO_4^{-2} (Table 3). Faé et al. (2011) report that freshly processed "slag" has a high pH, about 13.2 but this value decreases with "age" and stabilizes at about pH 11.2. In itself, this high level of alkalinity is sufficient to classify "slag" as toxic (Coya et al., 2000). Nevertheless, Pb leaching experiments showed (Table 4), that in a slightly acid environment, the "slag" is stable in the short term since the concentrations of Pb (4 mg L^{-1}) in the TCLP extract were below the permissible value (5 mg L^{-1}) established by Mexican legislation (NOM-052-SEMARNAT-2005). In contrast, the Pb concentration in the SPLP extract was 8 mg L^{-1} which exceeds the limits permitted suggesting that, under certain conditions, leaching from the "slag" can be an environmental hazard. Under normal conditions, the concentration of available Pb was relatively low; suggesting that ion exchange in the "slag" does not pose a large threat in the short term. However, it is difficult to predict the risks that may occur over the years (Coya et al., 2000; Faé et al., 2011).

The highest level of Pb pollution occurred southwest of the recovery plant (Table 5). Soil sampled along this transect was slightly alkaline (pH 7.5) and its EC ranged from 0.6 to 0.4 dS m^{-1} at 50 and 300 m, respectively. More salts were thus present in soil near the Pb recovery plant, probably because of dispersion of "slag" particles from the factory. Soil OM content was variable, with values of 5.3, 2.0 and 3.2% at 50,150 and 300 m, respectively, which coincided with the vegetation density. Since the soil was asandy to silty loam (NOM-021-SEMARNAT-2000), clay and OM would have the greatest influence on the CEC (Cala and Kunimine, 2003). The concentrations of Pb in the soil decreased with increasing distance from the factory, from 447 to 36 mg Pb kg^{-1} at 50 and 300 m, respectively (Table 6). In contrast, the levels of Ca and Na were relatively constant along the transect, but Fe levels mimicked those of Pb (Table 6). Similar situations have been reported by Farago et al. (1999) and Cala and Kunimine (2003). The reference value of Pb concentration in soils free of pollutants is approximately 13 mg kg^{-1} (Castillo et al., 2005). On this basis, Pb-contaminated soils have accumulated 34 fold more Pb than normal soils. Even soil samples collected 300 m from the plant exceeded reference values by 2.8 fold. Obviously, the distributions of Ca, Fe and Na do not pose the same threat as Pb to the environment.

In this particular area, dispersion of pollutants occurs in a predominantly southwest direction which coincides with the direction of the prevailing winds (Figure 2). This suggests that the population at risk is also located southwest from the recovery plant and the closest community is only about 0.5 km from the factory. In fact, workers from the plant under study already present high blood Pb concentrations (Quintanar-Escorza et al., 2007), indicating the need to regulate human settlements in areas surrounding the Pb recovery plant under study and/or to impose strict environmental standards on Pb smelters.

Alternative treatments, such as phytoremediation, have been reported as successful strategies to attenuate Pb contamination in soil (Trezena de Araújo and do Nascimento, 2010) and could be used for the recovery of

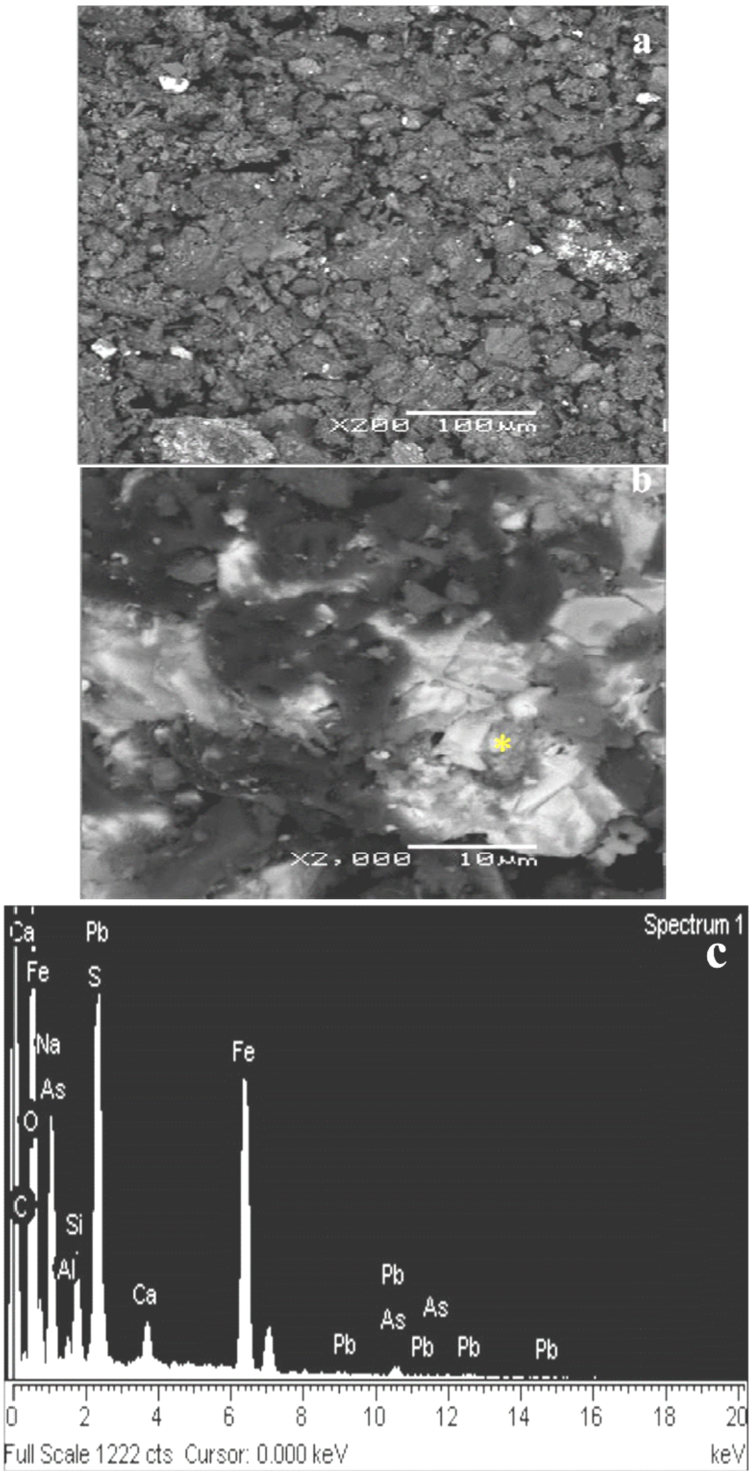

Figure 1. a-c Scanning electron microscopeimages of a Pb“slag” sample. (a) Magnified 200 times. (b) Magnified 2,000 times. Bars represent 100 µm and 10 µm, respectively. (c) EDS spectrum of a “white zone”* from Figure 1b.

areas adjacent to Pb-recovery plants.

Conclusions

High levels of PbO (3.4%), high pH (10) and increased EC (600 dS m^{-1}) in the “slag” are sufficient to consider this industrial waste as hazardous. In a moderately acid environment, as much as 8 mg Pb L^{-1} may be leached from the slag. This amount is well above the limits set by the Mexican legislation.

Hazardous concentrations of Pb, in the soil around the Pb recovery plant were found in the southwest area. The

Table 3. Chemical characteristics of Pb “slag”.

Property	**Content**
pH	10.1± 0.02
EC (dS m^{-1})	605.6± 4.04
Anions (mmol L^{-1}):	
CO_3^{-2}	1642.0 ± 8.48
HCO_3^-	59.0 ± 9.89
SO_4^{-2}	183.9 ±0.020

Table 4. Concentration of lead leached out of the Pb “slag” in leaching tests.

Test	**Pb (mg L^{-1})**
TCLP	4.0 ± 0.003
SPLP	8.0 ± 0.010
Available Pb	4.3 ± 0.020

Table 5. Soils properties southwest of the Pb recovery plant.

Distance (m)	**pH**	**EC**	**OM**	**Sand**	**Silt**	**Clay**	**CEC**
		(dS m^{-1})	**(%)**				**(cmol kg^{-1})**
50	7.2	0.6	5.3	52.9	36.6	10.5	30.1
150	7.5	0.5	2.0	36.9	50.6	12.5	45.9
300	7.7	0.4	3.2	36.9	50.6	12.5	43.1

Table 6. Total concentrations of metals in soil samples taken at three distances from the Pb recovery plant.

Direction	**Distance**	**Pb**	**Na**	**Ca**	**Fe**
	(m)	**(mg kg^{-1})**			
Southwest	50	447	427	8700	8200
	150	149	423	12300	10400
	300	36	521	8000	4000

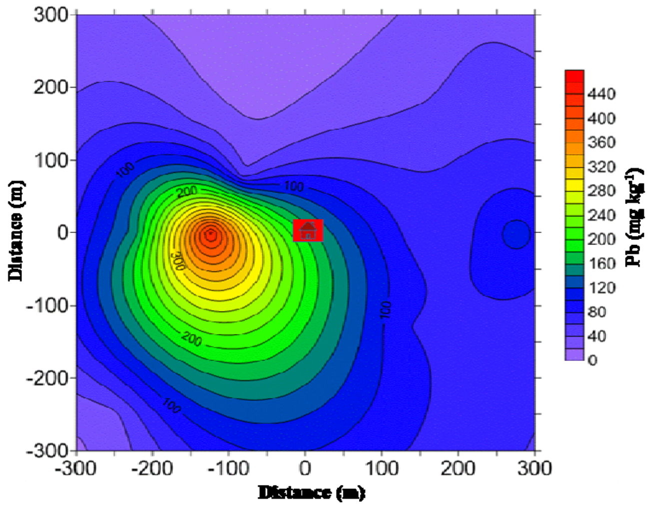

Figure 2. Superficial distribution of lead in a perimeter of 300 m around of the Pb recovery plant. Isocurves show the Pb concentration in soil. The coordinate (0, 0) indicates the location of the slag depositin the Pb recovery plant.

concentrations of Pb in soils decreased with increasing distance from the plant, being of 447, 149 and 36 mg Pb kg^{-1} at 50, 150 and 300 m, respectively. Due to these elevated Pb levels and to their easy dispersion into the environment, the health of human settlements in the area could be at risk.

Conflict of Interests

The author(s) have not declared any conflict of interests.

ACKNOWLEDGEMENTS

The authors wish to thank María Mondragón Sánchez and Juan M. Gutierrez for assistance in the scanning electron microscopy and in the preparation of isograms, respectively. We extend our thanks to Dr. W. Broughton for critical reading of this manuscript. We are also thankful to the SENESCYT-Ecuador scholarship program for grant support.

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