Full Length Research Paper

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

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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), SiO₂ (5.2), Na₂O (17.8), SO₃ (27.5) and Fe₂O₃ (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...
Table 1. Components of the Pb“slag” determined by X-ray fluorescence.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>0.056</td>
</tr>
<tr>
<td>PbO₂</td>
<td>0.084</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.104</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.110</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.121</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.142</td>
</tr>
<tr>
<td>Sr₂O₃</td>
<td>0.158</td>
</tr>
<tr>
<td>MgO</td>
<td>0.195</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>0.246</td>
</tr>
<tr>
<td>MnO</td>
<td>0.255</td>
</tr>
<tr>
<td>CuO</td>
<td>0.278</td>
</tr>
<tr>
<td>Cl</td>
<td>0.317</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.423</td>
</tr>
<tr>
<td>BaO</td>
<td>0.554</td>
</tr>
<tr>
<td>SnO₂</td>
<td>0.890</td>
</tr>
<tr>
<td>CaO</td>
<td>1.460</td>
</tr>
<tr>
<td>PbO</td>
<td>3.430</td>
</tr>
<tr>
<td>SiO₂</td>
<td>5.180</td>
</tr>
<tr>
<td>Na₂O</td>
<td>17.840</td>
</tr>
<tr>
<td>SO₃</td>
<td>27.450</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>40.740</td>
</tr>
</tbody>
</table>

The study site was a Pb recovery plant located in the State of Guanajuato, Mexico at 101° 41’ 00” west, 21° 07’ 22” north and an altitude of 1798 m. The smelter is dedicated to the recovery 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.

RESULTS AND DISCUSSION

The major compounds found in “slag” were: CaO, PbO, SiO₂, Na₂O, SO₃, and Fe₂O₃, 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 Bernardes, 2011). Table 2 summarizes the elemental analysis carried out by SEM-EDS and ICPAES. 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 NaHCO₃, Fe filings and mineral coal that are added to the molten during the melting
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 (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 (Yañez 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, resemble quartz grains. When enlarged, it is apparent that these "bright spots" possess defined structures with the above analogy with a macadamized surface, resembling quartz grains. When enlarged, it is apparent that these "bright spots" possess defined structures.

In aqueous solution, the "slag" is alkaline, with a high EC, high signal intensities correspond to elevated concentrations of elements with large atomic numbers and, thus, resemble quartz grains. When enlarged, it is apparent that these "bright spots" possess defined structures.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.38 ± 0.15a</td>
</tr>
<tr>
<td>As</td>
<td>0.52 ± 0.11a</td>
</tr>
<tr>
<td>C</td>
<td>7.19 ± 0.69a</td>
</tr>
<tr>
<td>Ca</td>
<td>1.57 ± 0.06a</td>
</tr>
<tr>
<td>Fe</td>
<td>23.28 ± 0.43a</td>
</tr>
<tr>
<td>Na</td>
<td>12.56 ± 0.38a</td>
</tr>
<tr>
<td>O</td>
<td>3.79 ± 0.40a</td>
</tr>
<tr>
<td>Pb</td>
<td>3.36 ± 0.29a</td>
</tr>
<tr>
<td>S</td>
<td>10.80 ± 0.16a</td>
</tr>
<tr>
<td>Si</td>
<td>2.78 ± 0.05a</td>
</tr>
<tr>
<td>Cd</td>
<td>0.04 ± 0.02b</td>
</tr>
<tr>
<td>Co</td>
<td>0.01 ± 0.01b</td>
</tr>
<tr>
<td>Ni</td>
<td>0.02 ± 0.03b</td>
</tr>
</tbody>
</table>

*SEM-EDS and ICP-AES methods.

A recent study (Coya et al., 2000; Faé et al., 2011) 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, resemble quartz grains. When enlarged, it is apparent that these "bright spots" possess defined structures. 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 4 mg L⁻¹ (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 Pb contamination.
Figure 1. a-c Scanning electron microscope images 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”.

<table>
<thead>
<tr>
<th>Property</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10.1 ± 0.02</td>
</tr>
<tr>
<td>EC (dS m⁻¹)</td>
<td>605.6 ± 4.04</td>
</tr>
</tbody>
</table>

Anions (mmol L⁻¹):
- \( \text{CO}_3^{2-} \): 1642.0 ± 8.48
- \( \text{HCO}_3^- \): 59.0 ± 9.89
- \( \text{SO}_4^{2-} \): 183.9 ± 0.020

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

<table>
<thead>
<tr>
<th>Test</th>
<th>Pb (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCLP</td>
<td>4.0 ± 0.003</td>
</tr>
<tr>
<td>SPLP</td>
<td>8.0 ± 0.010</td>
</tr>
<tr>
<td>Available Pb</td>
<td>4.3 ± 0.020</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Distance (m)</th>
<th>pH</th>
<th>EC (dS m⁻¹)</th>
<th>OM (%)</th>
<th>Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
<th>CEC (cmol kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>7.2</td>
<td>0.6</td>
<td>5.3</td>
<td>52.9</td>
<td>36.6</td>
<td>10.5</td>
<td>30.1</td>
</tr>
<tr>
<td>150</td>
<td>7.5</td>
<td>0.5</td>
<td>2.0</td>
<td>36.9</td>
<td>50.6</td>
<td>12.5</td>
<td>45.9</td>
</tr>
<tr>
<td>300</td>
<td>7.7</td>
<td>0.4</td>
<td>3.2</td>
<td>36.9</td>
<td>50.6</td>
<td>12.5</td>
<td>43.1</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Direction</th>
<th>Distance (m)</th>
<th>Pb (mg kg⁻¹)</th>
<th>Na (mg kg⁻¹)</th>
<th>Ca (mg kg⁻¹)</th>
<th>Fe (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SouthWest</td>
<td>50</td>
<td>447</td>
<td>427</td>
<td>8700</td>
<td>8200</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>149</td>
<td>423</td>
<td>12300</td>
<td>10400</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>36</td>
<td>521</td>
<td>8000</td>
<td>4000</td>
</tr>
</tbody>
</table>

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 deposit in 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.

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