THE ENVIRONMENTAL HAZARD CAUSED BY SMELTER SLAGS FROM THE STA. MARIA DE LA PAZ MINING DISTRICT IN MEXICO

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Abstract
The noxious potential of metallurgical tailings from the Ag/Pb/Zn/Cu mining district of Sta. Maria de la Paz (Mexico) is ascertained via the chemical characterization of slag material. Batch experiments using various extraction solutions (e.g. natural rainwater, water rich in humic substances, ammonium nitrate solution) revealed information on the dissolution behaviour of the elements Fe, Mn, Ni, Cu, Zn, As, Ba and Pb from slag with respect of grain size (slag material screened under 2 mm and analytically fine fraction) and elution time (2, 7.5, 24 and 240 h). An initial ecotoxicological assessment of the results is made and the environmental danger caused by large volumes of slag tailings is discussed. © 1998 Elsevier Science Ltd. All rights reserved

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INTRODUCTION
Over the past few years, numerous publications have reported on arsenic and heavy metal contamination in soils caused by mining activities. The majority of this pollution (which is often located in the vicinity of smelters), is the result of the deposition of metal oxides or tailings from the atmosphere (Little and Martin, 1972; Koning, 1974; Løberali and Steinnes, 1988; Puchelt, 1992). Contaminated sites can also be attributed to the considerable accumulation of slag and flotation material in soils (Simon, 1978; Gryschko et al., 1995), as has been found to be the case in the Black Forest region (Germany) and in La Paz (Mexico). The aforementioned research projects focused on investigations into heavy metal pollution in different compartments. In a second phase, several investigations were carried out with the aim of characterizing the mobility and availability of these substances from soils and slags (Castro, 1995; Manz, 1995; Castro et al., 1997).

In 1991–1995, extensive geochemical investigations were conducted in the mining district of Sta. Maria de La Paz in the Central Mexican Uplands in order to establish the potential risk to the environment created by mining activities (Castro, 1995). We decided to augment these findings by investigating the massive quantities of slag tailings originally stemming from the smelting of metal ore and still being present. In addition to geochemical characterization, a number of batch tests were also performed using different solvents. Various elution agents designed to emulate near-natural conditions enabled the mobilization behaviour of inorganic elements (arsenic and heavy metals) to be studied in relation to the extraction time and grain size of a variety of slag material (Manz, 1995). When considering the findings obtained, it must be stressed that slag is merely one of a number of contamination sources affecting the environment. The mining area's soil and vegetation contain high levels of pollutants introduced by atmospheric input and wastewater from past and present mining activities (due in no small part to the mine owner's lack of environmental awareness).
100°35'W and 23°37' and 23°44'N, about 500 km NNW to Mexico City (Fig. 1). It comprises an asymmetric north–south depression, whose deepest point is located about 2 km east of the town of Matehuala at an altitude of 1550 m above sea level. The small town of La Paz in the west lies at an altitude of 1800 m above sea level. The upland has a semiarid climate, with seasonal water-bearing brooks resulting from summer rain. Using the FAO classification, the soil types in the area range from calcic to gypsic xerosoles (FAO–Unesco, 1988). The mines and the dressing plant lie on the western edge of the area, near La Paz. It was here in the mid-18th century that Ag–Pb–Zn ore was discovered in hydrothermal veins, along with Cu–Au ore in scars. The ore has been worked from that time, virtually continuously. In 1992 the Ag–Pb–Zn mines were shut down as a reaction to the low prices on the international market; but the Cu–Au mines are still operating.

The ore was dressed by flotation and smelted in a plant on the northern edge of the mining district outside the town Matehuala (near H4 in Fig. 1) until the mid-1960s, when the plant was closed down. The ore was subsequently smelted and processed at other facilities elsewhere in Mexico or abroad.

This immense activity has resulted in many contaminated sites, the most significant of which are shown in Fig. 1, namely the flotation tailings (H1–H3) to the east of La Paz and a slag tailings heap measuring 400 m×250 m with a height of up to 8 m on the outskirts of Matehuala (H4). Nowadays, the former smelting area is undergoing redevelopment and some of the slag material has been used for road-metal, footpaths and railroad routes. The presence of huge quantities of tailings begs the question as to the precise environmental risk they pose.

MATERIAL AND METHODS

The slag tailings were sampled at different locations, the material subsequently being mixed to produce a composite sample weighing about 2 kg. Preparation involved the following stages:

1. Cleaning, screening and crushing to a grain size less than 2 mm;
2. Removal of secondary weathered fragments;
3. Homogenization of the whole material less than 2 mm;
4. Grinding of about half of the slag material in a planetary mill;
5. Secondary homogenization of the ground material.

In order to determine the total concentration of pollutants, the ground material was dissolved with HF–HNO₃–HClO₄ after Heinrichs and Herrmann (1990). The elements in the solution were determined using Inductively Coupled Plasma Source Mass Spectrometry.
photometric methods. Additional measurements were also made (X-ray fluorescence and neutron activation analysis) in order to evaluate the results. Batch experiments with a slag/solution ratio of 1:10 were performed in polyethylene bottles on a horizontal shake machine using both slag material under 2 mm and analytically fine material. As natural processes are not subject to constant pH, the batch tests were not carried out at a constant pH either. Several different eluents were used in the 24-h batch experiments:

1. Acidified demineralized H₂O (pH 1, standardized with HNO₃), to estimate the extractability of heavy metals under extremely aggressive conditions;
2. Natural rainwater (RW) with a pH of 5.4, to simulate near-natural leaching conditions;
3. Water rich in humic substances (HW) from an upland moor lake near Kaltenbronn in the Black Forest (Germany) with a pH of about 4, to simulate the concentration of humic substances in a soil solution;
4. A 1 M ammonium nitrate solution (NH₄NO₃) with a pH of 4.8—a method which has been used in Germany since 1995 for the extraction of available trace elements from soils (DIN 19730);
5. A solution of 0.25 g CaCO₃ in 1 litre bidistilled water with a pH of about 7 at the beginning of the batch test, to simulate the effect of a calcareous soil solution.

In addition, extensive time-dependent batch experiments (2, 7.5, 24 and 240 h) with rainwater, humic water and calcareous water were conducted on the screened material. Some batch tests were repeated to facilitate the evaluation of the results. For some metals (Cd, Cr, Sb and Bi) the concentrations in the eluates were often under the detection limit of the analytically method used.

RESULTS AND DISCUSSION

The area under investigation is characterized by high arsenic, lead, zinc, copper and cadmium pollution. The flotation residue and the slag are deposited in huge, unsecured tailings, and are consequently exposed to direct rainfall and wind erosion. Arsenic and heavy metals have accumulated in the mine water and the tailings seepage. This water reaches the preliminary clarifier virtually unaltered and may enter the groundwater. Moreover, the contaminated water is also used to irrigate vegetables and cereals (chiefly maize). This environmental risk has been highlighted by several investigations in the surrounding area (Castro, 1995).

Chemical characterization and pollution potential

In macroscopic terms, the basic glass slag has a colour ranging from black to greyish black and appears glassy, similar to an obsidian. It has a homogeneous dense structure and fractures sharply. The metallurgical residue of the tailings mainly has a particle size range with a diameter ranging from below 5 cm to an analytically fine fraction. Unsmelted ore material is sometimes encountered. Investigations using the microsonde on comparable slag invariably show that heavy metals can often be found drop-shaped inclusions in an oxide silicate ground mass. In some cases the heavy metals (e.g. zinc and lead) occur as silicates, which are formed under extremely high smelting temperatures (Faber, 1954; Bachmann, 1982; Manz, 1995).

In addition to high fractions of SiO₂, Fe₂O₃ and CaO, the main components also include high concentrations of a number of heavy metals, especially zinc (2.86%; Fig. 2). Various iron ores and limestone were added as flux during the smelting process. The unusually high levels of arsenic for slag of this type (0.38%) are remarkable, as most of the arsenic present usually escapes during the smelting process, as arsenic oxide. The slag's high arsenic concentration may be due to the type and efficiency of the smelting method used; alternatively it could be the result of the repeated addition of arsenic and heavy metal oxides accumulating in the condensing chamber during the roasting and smelting process. It can be seen in Fig. 2 that apart from arsenic, high concentrations of the environmentally significant elements Zn, Pb, Cu and Sb are also present in the metallurgical residue.

Results of the batch experiments

In order to determine the metal fractions which are soluble under extremely aggressive conditions, the slag (grain size < 2 mm) was eluted for 24 h with an eluate comprising a solution adjusted to a pH of 1 using HNO₃ (Table 1). These batch experiments were not conducted under constant pH conditions, and the values at the end of the experiment were approximately 4.4. The relatively low mobilization rates (concentrations in mg kg⁻¹ in Table 1, calculated on the basis of the original slag) of Cu, As, Sb and Pb may be attributed to the low solubilities of these compounds, under these pH conditions. Furthermore, metals already dissolved during the batch experiment were readsorbed on negatively charged slag surfaces, or specifically adsorbed, for example, to dissolved iron oxides. The high percentage concentration of Ni is remarkable, although the absolute concentrations dissolved are very low. It will be fixed to a cation exchange complex, because the main amounts can be released by ammonium nitrate.

One aim of the chemical analyses was to distinguish the quantities of As and heavy metals mobilized from different grain sizes. The screened (< 2 mm) and analytically fine ground slag material were shaken for 24 h with various elution agents (Figs 3 and 4). During the experiments, the concentrations in the eluates were frequently below the analytical detection limit and therefore some elements are ignored. Figure 3 shows the results of the batch experiments carried out on the screened material (grain size < 2 mm). The lowest
Fig. 2. Chemical composition of slag (main and some noxious trace elements). HM = Heavy metals and other components. * = Average levels in slag; the data were taken from various sources in the literature for comparable slags and the mean concentrations were calculated (Goldenberg, 1990, 1994).

Table 1. Mobilization of some elements from slag (grain size < 2 mm) using a HNO₃ solution, pH 1 (absolute and relative concentrations of dissolved metals are given)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Na</th>
<th>Mg</th>
<th>K</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute concentrations of dissolved metals (mg kg⁻¹)</td>
<td>449</td>
<td>414</td>
<td>14000</td>
<td>414</td>
<td>10300</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>Relative concentrations of dissolved metals (%)</td>
<td>2.47</td>
<td>7.02</td>
<td>6.89</td>
<td>9.28</td>
<td>5.67</td>
<td>25.82</td>
<td></td>
</tr>
<tr>
<td>Elements</td>
<td>Cu</td>
<td>Zn</td>
<td>As</td>
<td>Cd</td>
<td>Sb</td>
<td>Ba</td>
<td>Pb</td>
</tr>
<tr>
<td>Absolute concentrations of dissolved metals (mg kg⁻¹)</td>
<td>3.59</td>
<td>2736</td>
<td>5.55</td>
<td>0.45</td>
<td>0.15</td>
<td>112</td>
<td>18</td>
</tr>
<tr>
<td>Relative concentrations of dissolved metals (%)</td>
<td>0.16</td>
<td>9.55</td>
<td>0.15</td>
<td>3.78</td>
<td>0.03</td>
<td>5.17</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Fig. 3. Quantities and fractions of As and heavy metals which can be eluted from slag with a grain size < 2 mm using various elution agents (figures quoted in mg kg⁻¹ and as a percentage. RW: natural rainwater; HW: water rich in humic substances. Columns not shown = below detection limit; shaking time 24 h).

amounts were mobilized by the watery calcareous solution (Fe: 3.9 mg kg⁻¹, Zn: 2.3 mg kg⁻¹, As: 1.3 mg kg⁻¹); the largest quantities were mobilized by the 1 M ammonium nitrate solution (Cu: 142 mg kg⁻¹, Zn: 59.1 mg kg⁻¹, Pb: 18.8 mg kg⁻¹). Compared to total content in the slag, the maximum amount of any element dissolved by CaCO₃ was just 0.05% (Ba), in the same order of magnitude as the figures for HW (0.4%, Cu), and RW (0.07%, Pb and Ba). In contrast, NH₄NO₃ mobilized as much as 19% (Ni), although this hardly presents a risk owing to the low total content of Ni in the metallurgical residues. In the case of RW and HW, the concentrations in the eluates were actually below the detection limit. However, the situation is quite different with regard to the environmentally significant heavy metals and As, which are present in much higher fractions in the slag and are also mobilized in greater quantities. Nearly all the findings in Fig. 4 for analytically fine slag material reveal even larger quantities mobilized, for example 200 mg kg⁻¹ of Cu in the
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Fig. 4. Quantities and fractions of As and heavy metals which can be eluted from analytically fine slag material using various elution agents (figures quoted in mg kg⁻¹ and as a percentage. RW: natural rainwater; HW: water rich in humic substances. Columns not shown = below detection limit; shaking time 24 h).

Table 2. Ratios between amounts of heavy metal extracted from different grain sizes (finely ground < 2 mm) by various extraction agents (batch-time 24 h)

<table>
<thead>
<tr>
<th>Extraction agent</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Ba</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O with CaCO₃</td>
<td>1.06</td>
<td>1.25</td>
<td>—</td>
<td>0.40</td>
<td>0.70</td>
<td>1.49</td>
<td>3.65</td>
<td>0.73</td>
</tr>
<tr>
<td>Rainwater (RW)</td>
<td>1.81</td>
<td>2.50</td>
<td>—</td>
<td>0.99</td>
<td>1.64</td>
<td>1.92</td>
<td>1.31</td>
<td>0.35</td>
</tr>
<tr>
<td>Water rich on</td>
<td>1.27</td>
<td>3.11</td>
<td>—</td>
<td>1.27</td>
<td>1.51</td>
<td>1.09</td>
<td>1.23</td>
<td>0.67</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>3.37</td>
<td>—</td>
<td>0.83</td>
<td>1.34</td>
<td>1.98</td>
<td>0.48</td>
<td>2.07</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Difference extraction agents and fractions (crushed < 2 mm, analytically fine material) show different solubility sequences at the end of the batch test. The reason for this is that arsenic for example has a significantly higher solubility from its compounds in the face of a higher pH value. In Table 2 ratios of amounts extracted between the two different grain sizes are shown. With the exception of Pb and Cu, more heavy metals are mobilized from analytically fine material, as a result of its larger surface area, leading to a better attack by chemical action. In contrast the dissolved Pb can be trapped by newly formed hydrous iron oxides (Gadde and Laitinen, 1974).

The experiments with natural water rich in humic substances showed that very large quantities of certain heavy metals in the slag material can sometimes be mobilized (Figs 4 and 5). This extraction agent was used as it has a chemical composition similar (but more diluted) to that of moisture in the upper mineral soil horizon, and thus enables estimation of the order of magnitude in which pollutants may be available to plants for a short time before sorption onto various soil components in the 'soil solution'.

Slag with a grain size < 2 mm was used for the time-dependent batch experiments. Elution took place for 2, 7.5, 24 and 240 h using three different elution agents (RW, HW and NH₄NO₃). Once again, a constant solid-solution ratio of 1:10 (5 g slag to 50 ml extraction solution) was selected for each batch experiment. Despite the homogenization of the material, considerable fluctuations in concentration sometimes occurred, owing to the non-homogeneities in the slag (mainly when using the screened material). These could not be completely excluded, as the metallic inclusions in particular occurred with differing density, size and distribution.

The metals exhibit very different elution behaviour according to the use of extraction agents and with increasing elution time, which is chiefly due to the changing pH during the course of the experiment (Fig. 5). The rise in pH over time is most clearly apparent with the rainwater because of its low mineralization. In many cases, an equilibrium between the solid and dissolved phases was reached for the heavy metals after being shaken for just 24 h. In contrast, some elements failed to achieve equilibrium even after an extraction period lasting 240 h. In some batch experiments, the heavy metal content in the filtrate was actually observed to decrease with increasing elution time. This could be due to a number of reasons:

- The rising pH during the experiment;
- Exceedance of the solubility product of certain compounds;
- Increased adsorption of positively charged cations onto newly formed Fe hydroxides and oxyhydroxides, and thus removal from the eluate;
- Readsoption on the slag surface of the particles.

CRITICAL REVIEW AND PROSPECTS

The residues accumulating during ore processing, with their high levels of As, Pb, Zn and Cu, were dumped on open, unsecured slag-heaps, and were thus exposed to...
wind erosion and scattered over the region. Another environmental problem is caused by seepage water, which mobilizes the pollutants, can enter the river system and can contaminate the soil and groundwater (Castro, 1995). It has been demonstrated by analyzing maize and chili plants that the pollutants from the mine water and slag-heaps can accumulate in the human food chain. For example, it was discovered that the levels of As, which is usually present in non-accumulator plants in the order of 0.01–1.5 mg kg\(^{-1}\) dry weight (Bowen, 1979; Léonard, 1991), are exceeded many times over (Castro, 1995; Castro et al., 1996). Water leaking out at the base of the slag dump is used to irrigate water allotments and cornfields, thus adding to the transfer of pollutants to vegetation.

Wind erosion has played and continues to play a crucial role in the spread of pollutants, owing to the region’s semiarid climate. By the time the smelter was closed down in the mid-1960s, the majority of the arsenic (in the form of As\(_4\)O\(_6\)) and other pollutants had been emitted into the atmosphere. Depending on the dust mass, it condensed on particles with a diameter below 1 \(\mu\)m (Piver, 1983; Glooschenko and Arafat, 1988), and these particles could be transported over long distances. Another possible toxicological risk to humans can exist through the inhalation of PM 10s (particles with a diameter particles < 10 \(\mu\)m) containing high concentrations in arsenic and heavy metals. Toxicological and epidemiological studies are required to investigate the effects to humans.

The encapsulation of the slag-heaps and the installation of a drainage system to collect the polluted water is required to prevent the direct discharge of contamination via water. In addition, the slag should not be used for building roads or footpaths. However, the most important measure which should be tackled is to secure the flotation and slag-heaps, either by covering them with natural soil material followed by recultivation (in order to avoid erosion) or by sealing them with plastic sheeting. This would prevent the smallest particles from drifting over the surrounding district. In order to better assess the danger to the ecosystem emanating from the residues, supplementary ecotoxicological investigations are essential. These could be carried out indirectly in the form of further possible extraction methods already conducted on similar material (Kramer et al., 1988; Förstner et al., 1991; Gupta, 1991) or directly via toxicological tests on salt extracts (Lätsch et al., 1991).

REFERENCES


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