

Article

Effect of Sludge Amendment on Remediation of Metal Contaminated Soils

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Abstract: Column-leaching and pilot-scale experiments were conducted to evaluate the use of biosolids (sewage sludges) to control the mobilization of metals from contaminated soils with smelting slags. The pilot-scale experiments using amended soils showed that Cu, Pb and Sb were retained, decreasing their concentrations from 250 µg/L, 80 µg/L and 6 µg/L, respectively in the leachates of contaminated soils, to <20 µg/L, 40 µg/L and 4 µg/L, respectively, in the amended material. Hydrogeochemical modeling of the leachates using Minteq revealed that the degree of complexation of Cu rose 56.3% and 57.6% in leachates of amended soils. Moreover, Cu may be immobilized by biosolids, possibly via adsorption by oxyhydroxides of Fe or sorption by organic matter. The partial retention of Pb coincides with the possible precipitation of chloropyromorphite, which is the most stable mineral phase in the pH-Eh conditions of the leachates from the amended material. The retention of Sb may be associated with the precipitation of Sb₂O₃, which is the most stable mineral phase in the experimental conditions. The organic amendments used in this study increased some metal and metalloid concentrations in the leachates (Fe, Mn, Ni, As and Se), which suggests that the organic amendments could be used with caution to remediate metal contaminated areas.

Keywords: contaminated soil; leachates; biosolids; metals

1. Introduction

Soils contaminated with smelting wastes have traditionally been considered poor reactive materials because the potential contaminants are encapsulated in low-solubility compounds such as silicates,

oxides and glassy forms [1,2]. However, smelter slags are reactive and may be the source of metals such as Ag, As, Ba, Cd, Cu, Pb, Sb and Zn in stream, soil and groundwater contamination [3–12].

Thus, base-metal slag deposits at the Penn Mine in California contained relatively high concentrations of As, Ba, Cd, Cu, Pb and Zn, which were hosted by different types of phases [13]. Geochemical modeling of field and laboratory data indicated that the main processes controlling dissolved metal concentrations were dissolution of fayalite, willemite and glass, sulfide oxidation, and secondary phases, which suggests that the dissolved concentrations of Al, Ba, Cu, Mn, SiO₂, and SO₄ may be controlled by mineral solubilities. Also, secondary minerals appeared as coatings on surfaces and as precipitates of amorphous Fe, Al oxyhydroxides, chalcanthite, siderotil, jarosite, brochantite and gypsum [7] and may control the mobility of metals to soil and water bodies.

The use of organic amendments as reactive materials may control metal mobilization [14,15] and aid the reclamation of contaminated soils at smelting sites, since such areas typically lack natural vegetation and have other deficiencies [16]. In addition, reactive layers containing labile organic carbon may promote bacterially mediated sulfate reduction reactions and the removal of sulfate and dissolved metals from contaminated acid mine drainages [17]. Organic amendments from municipal solid waste compost have been used in the reclamation of mine spoils from limestone quarries [18]. In addition, sugar foam waste has been applied to red soils [19] in a semiarid environment similar to the study area conditions.

Basta *et al.* [20] showed the effectiveness of lime-stabilized biosolids at reducing the extractability and bioavailability of Cd, Pb and Zn from smelter-contaminated soils, and indicated that alkaline organic treatments reduced metal extractability and phytoavailability.

The use of sewage sludge on sulfide mine tailings is based on supplying nutrients to promote plant growth [21,22] and thus increasing biomass production [23]. The availability of metals after the application of sludge to tailings deposits has also been observed [24]. Some studies showed an increase in sulfide oxidation or reductive dissolution reactions in mine waste [25,26] and the release of metals. In addition, the application of polylactic acid amendments to smelter tailings increased the bioavailability of Pb, Ni and Zn [27]. The use of manure compost and sewage sludge on Pb/Zn tailings led to a decrease in pH, an increase in electrical conductivity (EC) and in extractable Cu, and a decrease in extractable Pb and Zn [28]. Ni mobilization due to the formation of organic complexes from sewage sludge may be environmentally significant because of the relatively poor retention of Ni by the sludge [29]. The use of column experiments and the application of organic amendments such as cattle manure on mine tailings have also shown the mobilization of heavy metals (Zn, Cd, Pb) by the leaching of Pb-Zn mine waste [16].

Laboratory studies in which biosolids were applied to Pb-Ag mine tailings showed that Fe, Mn, Zn and Pb were removed and Cu and Ni mobilized. Experiments carried out on Pb-Fe tailings produced similar results, in which Cu, Pb, Fe and Mn were retained and Ni and Zn mobilized [15]. In addition, composted sludge has been shown to have a high affinity for metals such as Pb [30]. Furthermore, Park *et al.* [31] showed that low metal organic amendments could be used as a sink for reducing the bioavailability of metals in contaminated soils. In one current treatment technique, an organic carbon reactive material is used to stimulate sulfate reduction and the subsequent metal sulfide precipitation [32].

The reduction of sulfates by organic carbon may take the following form:



The H₂S that is generated, the Fe (II) and other metallic species such as As, Cd, Co, Cu, Ni, Pb and Zn may precipitate, thereby producing sulfide minerals:



The main objectives of this study were to evaluate how organic amendments affect metal mobility from contaminated soils with smelter slags and evaluate the possible remediation of extensive contaminated areas, which are the source of metal mobilization.

2. Materials and Methods

2.1. Research Site

The area comprising the Sierra Almagrera (Figure 1), located 90 km NE of the city of Almería (SE Spain), together with the Iberian Pyrite Belt and the Cartagena mining district, is the oldest metallurgical and mining area in the Iberian Peninsula [33–35]. During the nineteenth century and the early twentieth century, the smelting plants located along the Mediterranean coastline of the Sierra Almagrera district produced approximately 550,000 t of Pb and 3000 t of Ag. The Sierra Almagrera area is located in a semi-arid region that is characterized by a highly irregular hydrological regime with long dry periods and intermittent periods of rainfall, in which the volume of precipitation in a few hours can exceed the annual average. The study area is close to the shoreline in the coastal part of the Sierra Almagrera, where the main slag dumps were generated between 1850 and 1885 (Figure 1). The waste deposits are now covered by anthropogenic soils and industrial facilities built over part of the metallurgical slags, which were partially used in the road construction. The site covers an area of approximately 120,000 m² and has a simple geological structure that comprises a metamorphic basement (phyllites and schists), a level of weathered phyllites, layers of smelter slags, and topsoil mixed with other waste. The study area, which is now used for industrial activities, contains a 4–5 m deep unconfined aquifer. The 2 m deep saturated zone is related to levels established by old smelter slags and/or colluvial deposits.

An important environmental concern related with these contaminated areas is associated with the damage of *Posidonia Oceanica* prairies in the coastal area [36], and the presence of significative contents of metals in the superficial marine sediments. Since *Posidonia Oceanica* is a seagrass endemic to Mediterranean Sea and is protected by the European laws, the conservation of this seagrass and, therefore, the control of metal contamination in the terrestrial source-areas may be of environmental concern in the old mining areas of SE Spain. The detailed characterization of the slags dumped in this area was described by Navarro *et al.* [9].

Figure 1. (a) Location of the study area and regional Geology. NQ: Neogene and Quaternary; UM: Volcanic-shoshonitic rocks of Miocene age; PT: Metamorphic basement; F: Main fractures. (b) Detail of smelting slags dumps in Sierra Almagrera (Almería, Spain). (c) Detail of the experimental device.

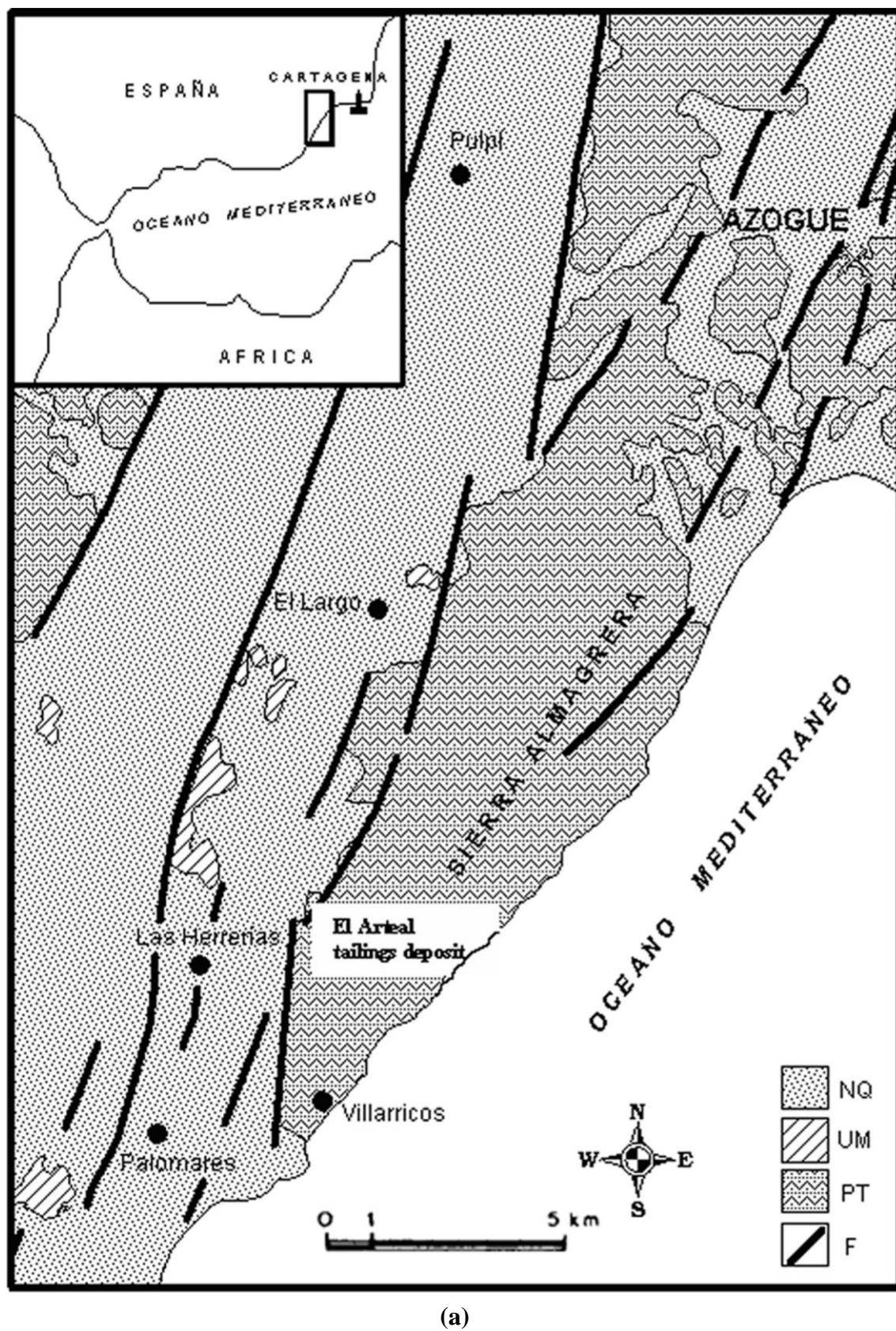


Figure 1. *Cont.*

(b)



(c)

2.2. Organic Amendments

The sewage sludge used is a stabilized biosolid from a depuration process in which seawater was used to eliminate organic matter from pharmaceutical waste waters. The sewage sludge showed a grain size distribution that was dominated by fine particles (94%–98%), an elevated content of organic matter (6.2%–13%) and a high content of soluble salts and gypsum (Table 1). Other physical parameters of the biosolid were a low dry density and a high degree of saturation.

In addition, the mechanical properties of sewage sludge were determined from soil laboratory tests. Thus, Atterberg limits were calculated showing a liquid limit of 60.8–65.4, a plastic limit of 59.1–60.0 and a plasticity index of 0.8–6.2 (Table 1). Besides, the air-dried compacted sludge was tested in vane shear assays, showing an effective angle of shearing resistance of 29.2–30.3, below the values obtained in similar experiences [37]. The sewage sludge had a high content of Ca (17.7%), S (5.28%), Mg (0.74%), P (5.71%) and particularly Na (1.38%), possibly due to the use of seawater in the treatment process that created the sludge. The metal content in the sludge was very low (Table 2), except for V (142 mg/kg). The amounts of As (9.9 mg/kg), Cd (0.5 mg/kg), Cu (12 mg/kg), Fe (7900 mg/kg), Pb (7 mg/kg) and Zn (78 mg/kg) were close to the concentrations detected in non-contaminated soils in the nearby region (Table 2). However, concentrations of Ba and Ni are above the values detected in the non-contaminated soils. The metal content of the sludge did not exceed the limits imposed by Spanish environmental regulations (RD 13-10/1990) for the total metal content in sewage sludge used on agricultural land and are above the Netherlands Soil Contamination Guidelines (intervention values).

2.3. Contaminated Soils and Smelting Slags

The total amount of metals and trace elements was analyzed by Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Au, Ag, As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, Ir, La, Lu, Na, Ni, Nd, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Th, Tb, U, W, Y and Yb were found by INAA, and Mo, Cu, Pb, Zn, Ag, Ni, Mn, Sr, Cd, Bi, V, Ca, P, Mg, Tl, Al, K, Y and Be were found by ICP-OES.

Previously, the mineralogy of soils and some slags was examined under a binocular microscope and analyzed using X-ray powder diffraction (XRD) at Actlabs (Ontario, Canada) and the Autonomous University of Barcelona (UAB).

Contaminated soils and smelting slags used in the leaching experiments showed high concentrations of Ag (46.1 mg/kg), As (51.6 mg/kg), Ba (101,000 mg/kg), Cu (227 mg/kg), Fe (20.4%), Mn (10,600 mg/kg), Pb (4900 mg/kg), Sb (243 mg/kg) and Zn (5070 mg/kg) (Table 2).

The slags were composed mainly of quartz, fayalite, barite, orthoclase and Zn-Pb-Fe alloys. In addition, the following weathering-related secondary phases were detected: jarosite-natrogjarosite, corrensite, ferrihydrite, kastningite and wuestite. No significant glass phases were detected in previous analyzed slags [9]. In addition, previous hydrogeochemical data showed that groundwater in the area had been contaminated by Cu, Fe, Mn, Pb, Zn and As to maximum concentrations of 0.64 mg/L Cu, 40 mg/L Fe, 0.6 mg/L Mn, 7.6 mg/L Zn, 5.1 mg/L Pb and 0.019 mg/L As [9]. Differences in the geochemical composition between the historically analyzed slags [9] and the slags used in the experiments may reflect the variation in furnace charges and smelting conditions over time [6].

Table 1. Main characteristics of biosolid (sewage sludge) used in the experiments.

Sample	Gravel (%)	Sand (%)	Fine Sand (%)	Fines (%)	Organic Matter (%)	Soluble Salts (%)	Gypsum (%)	W (%)	ρ_s	ρ_p	e_0	S (%)	W_L	W_P	I_p
M01	0	0	2	98	13	29.55	32.78	112.5	0.61	2.3	2.78	93.0	60.8	60.0	0.8
M02	0	0	6	94	6.2	24.7*	-	41.67	1.09	2.41	-	-	65.4	59.1	6.2

Gravel: $d_e > 5$ mm; Sand: $d_e > 2$ mm; Fine sand: $d_e > 0.08$ mm; Fines: $d_e < 0.08$ mm; W: biosolid wetness; ρ_s : dry density (g/cm^3); ρ_p : particle density (g/cm^3); e_0 : void ratio; S: degree of saturation; *: including gypsum; W_L : liquid limit; W_P : plastic limit; I_p : plasticity index.

Table 2. Geochemical composition of biosolid, and contaminated materials (contaminated soils P1 to P4 and smelting slags) used in the leaching experiments. Values in mg/kg, except Au (ppb) and Fe (%).

Material	Au	Ag	Cu	Cd	Mo	Pb	Ni	Zn	As	Ba	Co	Cr	Fe	Hg	Mn	Sb	Se	V
Biosolid	<2	0.3	12	0.5	2	7	39	78	9.9	540	3	40	0.79	<1	62	2.8	<3	142
P1-A	<2	<0.3	20	1.9	<1	97	57	227	34.9	900	18	139	6.29	<1	489	4.7	<3	142
P1-B	<2	<0.3	20	1.8	<1	508	43	122	87.1	660	19	102	4.97	<1	417	16.5	<3	64
P2-A	<2	0.4	22	12	1	2450	33	157	278	850	10	100	3.93	<1	358	40.8	<3	110
P2-B	<2	0.6	23	8.8	<1	2390	28	110	324	580	10	88	3.63	<1	358	47.3	<3	102
P3-A	<2	0.6	27	7.6	2	4900	39	192	337	1030	15	105	4.39	<1	469	63.4	<3	129
3-B	<2	<0.3	33	8.5	<1	2440	49	229	367	690	18	126	5.19	<1	457	34.2	<3	162
P4-A	<2	<0.3	30	0.6	<1	73	41	112	31.3	690	13	82	3.45	<1	571	4.9	<3	107
P4-B	<2	<0.3	34	1.4	<1	67	52	125	60.5	530	16	117	5.18	<1	513	7.8	<3	142
Smelting slags	<2	46.1	227	0.6	18	4460	17	5070	51.6	10.1*	10	40	20.4	<1	1.0*	243	<3	87
NCS	3	<0.4	15	<0.5	<1	17	26	57	16	310	8	55	2.69	<1	136	1.8	<3	96
NSGS	--	--	190	12	200	530	210	720	55	625	240	380	--	10	--	15	--	--

NCS: non contaminated soils developed over metamorphic materials in the nearby area; NSGS: Netherlands Soil Contamination Guidelines (intervention values); *: %.

2.4. Column Leaching Experiments

A leaching experiment was conducted in order to characterize the behavior of biosolid and the mobility of their components. The experiment comprised a column test consisted of a water reservoir, a peristaltic pump, a methacrylate column, and a series of instruments for determining some parameters of the effluents *in situ*, such as pH, Eh, EC (electrical conductivity), temperature and dissolved O₂. The column was made in a methacrylate cylinder, thus allowing for visual examination of the progress of the wetting front and detection of preferential flow channels along the column walls. The column was 750 mm long, with an outer diameter of 150 mm and a thickness of 5 mm [15,38].

Low mineralized water (LMW) entered the column through an injection system connected to a metering pump, which emitted a maximum flow of 10 L h⁻¹. The chemical characteristics of LMW are shown in Table 3. A constant-head reservoir was used to deliver influent water at a flow rate of 2.4 L h⁻¹. The inflow fluid was low mineralization water, which approximates the behavior of rainwater when it comes into contact with the waste in environmental conditions (Table 3). The samples were collected at the bottom of the column as a function of time. The first sample, which corresponds to time 0, was taken when water started to flow from the lower part of the column. The flow, pH and EC (electrical conductivity) were measured immediately after the sample was collected. The number of pore volumes reached in the column experiments is given by the following expression:

$$T_a = V t L^{-1} \quad (3)$$

where T_a is the number of pore volumes, V the pore velocity, L the column length and t the leaching time. In the column experiment, the final T_a was 4.7 pore volumes, which indicates a time period that can be considered as representative.

Table 3. Chemical composition of fluids from column leaching experiment with biosolid.

Values in µg/L.

Samples	PV	Cu	Pb	Sb	As	Se	Mn	Ni	EC (µS/cm)	Cl (mg/L)	SO ₄ (mg/L)
SL-1	0	178	<0.1	0.59	28.1	<0.2	274	161	5860	570	980
SL-2	0.45	13	134	0.25	5.59	1.3	9.8	14	-	-	-
SL-3	0.9	9.3	<0.1	0.21	5.31	0.5	5.4	5.5	-	-	-
SL-4	1.35	4.8	<0.1	0.23	4.09	<0.2	7.9	2.2	-	-	-
SL-5	1.8	9.6	<0.1	0.19	4.21	<0.2	3.3	1.8	-	-	-
SL-6	2.2	2.7	<0.1	0.16	3.17	<0.2	2.4	1.9	-	-	-
SL-7	2.7	1.6	<0.1	0.16	2.5	<0.2	1.4	0.5	-	-	-
SL-8	3.4	2.4	<0.1	0.13	2.2	<0.2	2.8	0.7	-	-	-
SL-9	4.0	1.5	<0.1	0.11	2.02	<0.2	1.1	0.4	-	-	-
SL-10	4.7	6.5	<0.1	0.12	1.89	<0.2	1.5	0.4	-	-	-
LMW	-	<0.2	0.1	0.02	0.34	<0.2	<0.1	<0.3	250	5.6	11.1

SL: sewage sludge leachates; LMW: low mineralized water used in the column leaching tests;

PV: number of pore volumes.

2.5. Pilot-Scale Experiments

The experimental device covered a surface of 30 m² approximately, divided into two sub-areas of 15 m²: an area of not-amended materials leaching, and an area of leaching of contaminated materials and organic amendments. These amendments comprised about 10% by weight of total soil and slags used in the experiment. The experimental system was fed by low mineralized water (LMW) (Tables 4 and 5) for 24 h with a constant flow rate of 5 L h⁻¹. The materials were laid over a low hydraulic conductivity liner (HDEP) with a slope of approximately 5%, to facilitate the leachate movement.

The LMW was introduced in the top of the experimental cells and flowed by means of a trickle irrigation system, which divided the total flow rate into several points of water recharge. The leachate sampling device comprised a narrow channel located in the lower area of each experimental sub-cell leaching, where the leachates were sampled with the aid of a syringe. We measured the pH, redox potential (Eh; mV), temperature, and EC ($\mu\text{S}/\text{cm}$) in the leachates *in situ* using portable devices, and corrected the values using standard solutions (HACH sensION TM378). The samples were filtered using a cellulose nitrate membrane with a pore size of 0.45 μm . The samples for cation analysis were later acidified to pH<2.0 by adding ultra-pure HNO₃. The samples were collected in 110 mL high-density polypropylene bottles, which were sealed with a double cap and stored in a refrigerator until analysis.

The cation concentrations were measured using inductively coupled plasma mass spectroscopy (ICP-MS) at ACTLABS (Ontario, Canada). The concentrations of chloride, nitrate and sulfate (in a second, untreated sample) were analyzed by ion chromatography. The alkalinity of the waters was analyzed by titration. The standard reference material NIST 1640 (ICP-MS) was used to evaluate accuracy.

To assess the potential role of organic matter in the mobility of metals, we used the Visual Minteq numerical code [39]. Visual Minteq includes a submodel for estimations of the complexation of metals with dissolved organic matter, which assumes that the composite ligand consists of a population of discrete binding sites in which the probability of occurrence of a binding site is normally distributed (Gaussian model) with respect to its log K value for proton or metal binding [40].

3. Results and Discussion

3.1. Column-Leaching Experiments

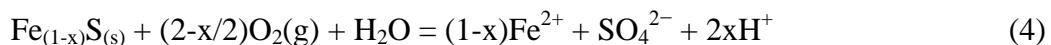
The first experiment comprised the leaching of “pure” biosolid to evaluate the possible mobility of the main anions and metals. The results showed low leaching of metals, except Ni, possibly because of the content of this metal in the sewage sludge (Table 2). We also found a significative concentrations of As (sample SL-1) and Pb (sample SL-2, Table 3). The high value of EC, chloride and sulphate detected may be associated with the origin of the water (seawater) used in the treatment processes that generated the sewage sludge.

3.2. Pilot-Scale Experiments

The results of leaching of not-amended materials (Table 4) showed mobilization of Cu (>0.2 mg/L), Fe (<1–2.0 mg/L), Mn (0.09–0.45 mg/L), Pb (0.02–0.08 mg/L) and Sb (6–7.5 $\mu\text{g}/\text{L}$) and other inorganic compounds (Ca, Na, Mg, and K). In addition, minor concentrations of As (4.0–7.5 $\mu\text{g}/\text{L}$), Se (<20 $\mu\text{g}/\text{L}$) and Cd (<1.0–2.0 $\mu\text{g}/\text{L}$) were detected. The concentrations of dissolved metals are similar to other slag

dumps [6,7,13] suggesting that the slags in the study area may mobilize significative metal amounts that can be released into the environment.

This indicates that contaminated soils and abandoned slags have high potential leachability (Tables 4 and 5). Major-element leachability may be associated with silicates and sulfides, and originated, possibly, due to the oxidation of pyrrhotite and the weathering of detected fayalite, melilite and celsian. The oxidation of pyrrhotite may mobilize Fe and SO₄ and decrease the pH of the pore water:



However, the weathering of olivine (mainly fayalite) may also mobilize Fe and Mg:



The high content of Mn (3.35%) and ZnO (1.34%) in olivine [9] may explain the high concentration of these elements in the leaching test. In addition, the weathering of K-feldspar detected in the slags may mobilize K and some metals after the dissolution of kaolinite:



Moreover, the weathering of melilite (Ca_{0.7}Ba_{0.4}Na_{0.3}Sr_{0.1}Zn_{0.1}Fe³⁺_{1.1}Al_{0.1}Si₂O₇) and celsian (BaAl₂Si₂O₈) may also explain the mobilization of Ca, Na, K and Zn. Besides, the presence of Pb may result from the presence of cotunnite and rich Sb-galena remainders in the slags. In the cell experiment with amended materials Cu, Pb and Sb were removed, however selected metals (Fe, Mn, and Ni) and metalloids (As, Se) were leached. The presence of metalloids (As, Se) in the leachates may be due to the high content of these elements in the slags (Table 2). Besides, the leaching of amended materials showed an increase of Ca, Mg, K and Na (Table 4) which could due to the origin of the biosolid (seawater) and the high content of these metals in the sewage sludge, which reached concentrations of 17.7% of Ca, 1.38% of Na and 0.74% of Mg (Table 2). In addition, organic acids and their anions may affect the weathering and dissolution rates of minerals such as feldspar and olivine [41,42]. Organic matter oxidation may therefore promote silicate weathering and kaolinite dissolution:



Thus, leachates of contaminated soils and slags with biosolid showed a decrease in pH and redox potential (Table 4). Furthermore, the bicarbonate increase (Table 5) can be attributed to the reaction of silicates with CO₂ and water [5] and possible carbonate buffering:



However, the leachability of each metal was very different in the leachates of amended materials, in which As, Se, Ni and Mn were mobilized, and Cu, Pb and Sb were retained. Figures 2 and 3 show the retention of Cu, Pb and Sb in the pilot-scale experiment, with the exception of Pb, which mobilized at the end of the leaching experiment. Although the removal of these elements may be caused by adsorption and/or co-precipitation involving the organic matter of sewage sludge, As and Se (Figure 4) were mobilized, possibly because of the pH-Eh conditions produced by biosolid addition. Thus, an increase in pH causes the anionic forms of As to be desorbed from solid phases.

Table 4. *In situ* determinations and metal concentrations of leachates of pilot-scale experiments. Values in µg/L; Eh: mV.

Analyte Symbol	t(min)	pH	Eh	Ca	Mg	K	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Cd	Sb	Ba	Pb
Unit				mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	
DL				0.7	0.001	0.03	0.5	0.1	10	0.005	0.3	0.2	0.5	0.03	0.2	0.01	0.01	0.1	0.01
E-1	0	7.68	-55	349	84.3	31.9	<50	290	<1,000	3.1	<30	250	<50	6	<20	1	6	70	80
E-2	30	7.74	-59	374	80.7	26.2	<50	220	<1,000	2.1	<30	220	<50	6	<20	1	6	60	50
E-3	90	7.68	-55	458	115	41.5	<50	450	<1,000	4.85	30	485	<50	7.5	<20	2	7.5	60	80
E-4	150	7.80	-62	378	79.6	23.1	240	260	2,500	2.9	<30	280	<50	7	<20	1	7	40	50
E-5	210	8.03	-75	339	61.1	13.4	<50	170	<1,000	2.7	<30	200	<50	7	<20	1	7	40	30
E-6	1,380	8.03	-76	351	54.8	12.3	<50	150	<1,000	1.4	<30	190	<50	4	<20	<1	7	30	20
E-7	1,440	8.03	-83	301	53.2	7.2	<50	90	<1,000	1.1	<30	70	<50	5	<20	<1	6	20	20
LE-1	0	7.43	-42	757	640	367	<50	450	2,100	12.9	100	<20	<50	34	100	<1	4	60	40
LE-3	90	7.34	-36	865	903	524	<50	500	2,700	19.1	150	<20	<50	37	30	4	5	30	60
LE-4	150	7.23	-30	867	945	566	<50	500	2,400	18.9	160	20	<50	44	60	2	5	40	70
LE-5	210	7.25	-31	721	572	337	130	390	3,700	12.7	90	<20	<50	38	50	2	4	10	30
LE-6	1,380	7.37	-38	796	724	398	<50	450	5,000	15.8	120	40	<50	32	30	<1	5	110	130
LE-7	1,440	7.40	-40	623	382	208	1760	460	14,300	10.7	80	70	<50	25	40	1	4	10	30
LMW	-	7.40	128	115	43.5	3.1	190	30	180	<0.5	<30	<20	<50	<3	<20	<1	1	30	<1
C₀	-	-	-	-	-	-	100	-	-	-	120	600	1,200	60	40	20	100	4,000	150

LMW: low mineralized water used in the pilot-scale experiments; DL: detection limit; C₀: European limits concentrations for leachates of inert wastes (percolation assay); E-1 to E-7: leachates of contaminated soils and slags; LE-1 to LE-7: leachates of amended materials.

Table 5. Main anions of leachates of pilot-scale experiments. DL: detection limit. Values in mg/L.

Analyte Symbol	t (min)	F	Cl	NO ₂ (as N)	Br	NO ₃ (as N)	PO ₄ (as P)	SO ₄	CO ₃ (²⁻)	HCO ₃ (⁻)
Unit		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
DL		0.01	0.03	0.01	0.03	0.01	0.02	0.03	1	1
E-1	0	0.65	1,160	<0.3	2.94	16.2	<0.5	1,550	<1	222
E-2	30	0.72	531	<0.1	1.46	9.37	0.42	1,320	<1	137
E-4	150	0.72	478	0.22	1.34	3.58	0.43	1,380	<1	135
E-6	1,380	0.72	282	<0.1	1.41	1.97	0.69	1,300	<1	114
E-7	1,440	0.58	244	0.91	1.03	2.13	0.6	1,140	<1	104
LE-1	0	<1	9,490	<1	26.9	277	4.72	4,420	<1	327
LE-3	90	<2	14,300	<2	23.4	384	5.44	5,220	<1	531
LE-4	150	<1	13,400	<1	38.6	355	4.92	5,420	<1	542
LE-5	210	<2	10,100	<2	14.2	267	3.07	4,710	<1	460
LE-6	1,380	<1	10,700	<1	18.2	207	4.62	5,330	<1	437
LE-7	1,440	<1	8,540	<1	23.2	185	5.2	4,840	<1	333
LMW	-	0.32	185	<0.04	1.58	0.3	<0.08	450	<1	131

LMW: low mineralized water used in the leaching experiments; E-1 to E-7: leachates of contaminated soils and slags; LE-1 to LE-7: leachates of amended materials.

Figure 2. Evolution of Cu and Ba in the pilot-scale experiments. Values in $\mu\text{g/L}$. Cu/Ba-S: change of Cu and Ba content in time, measured in effluent solution of not-amended experiment; Cu/Ba-S-SW: change of Cu and Ba content in time, measured in effluent solution of amended experiment.

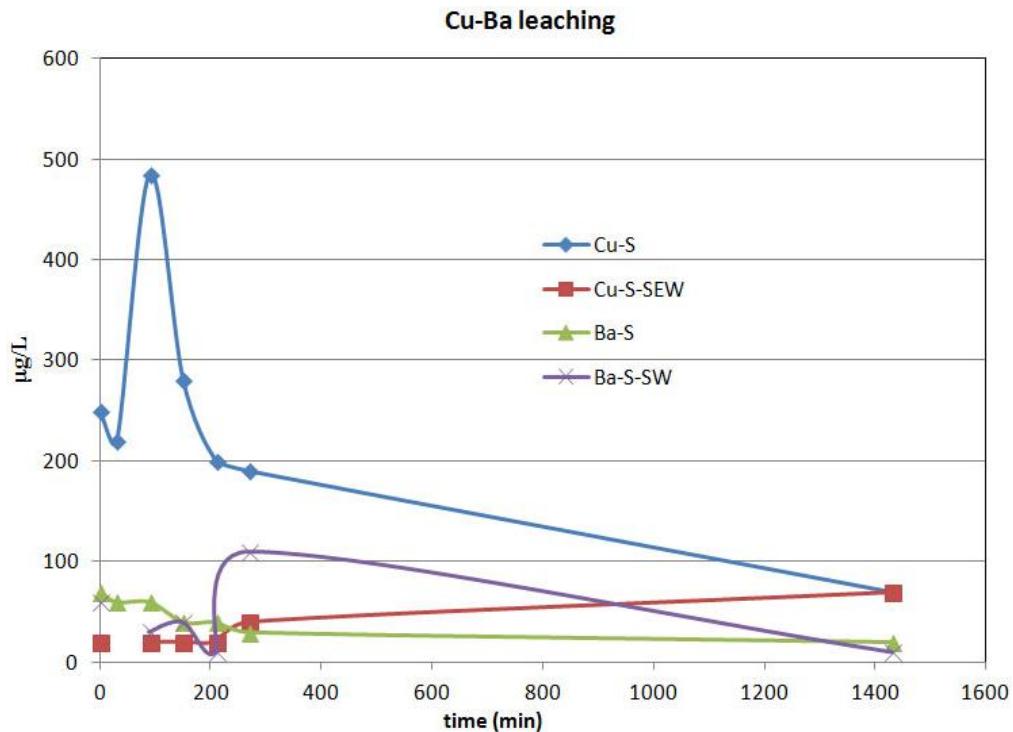


Figure 3. Evolution of Pb and Sb in the pilot-scale experiments. Values in $\mu\text{g/L}$. Pb/Sb-S: change of Pb and Sb content in time, measured in effluent solution of not-amended experiment; Pb/Sb-S-SW: change of Pb and Sb content in time, measured in effluent solution of amended experiment.

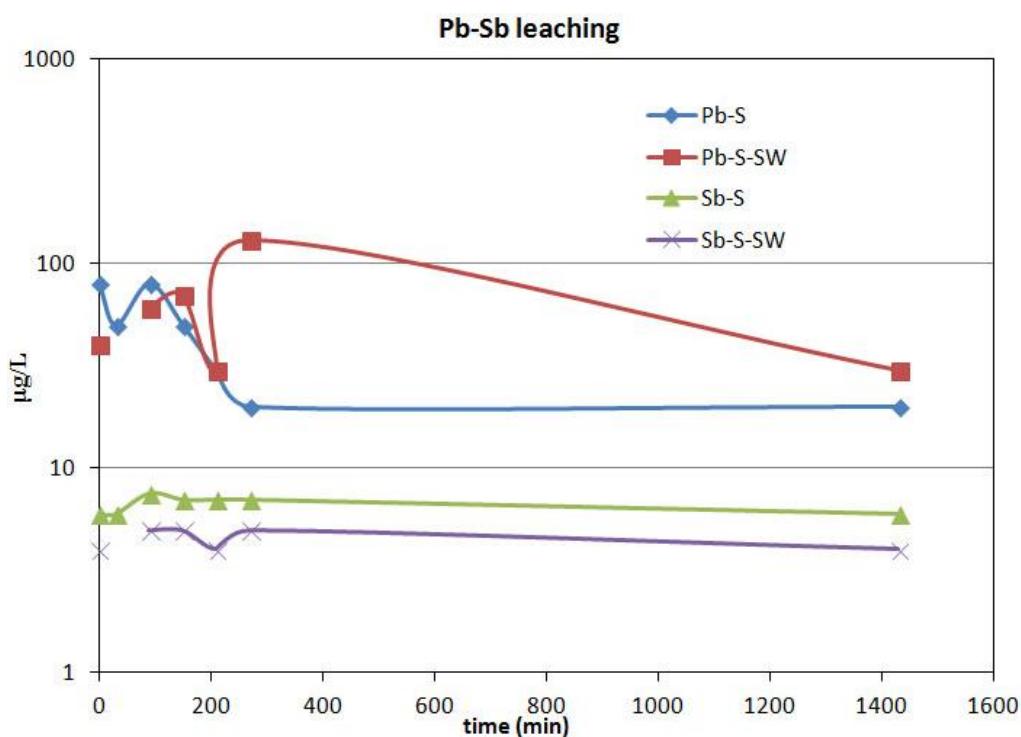
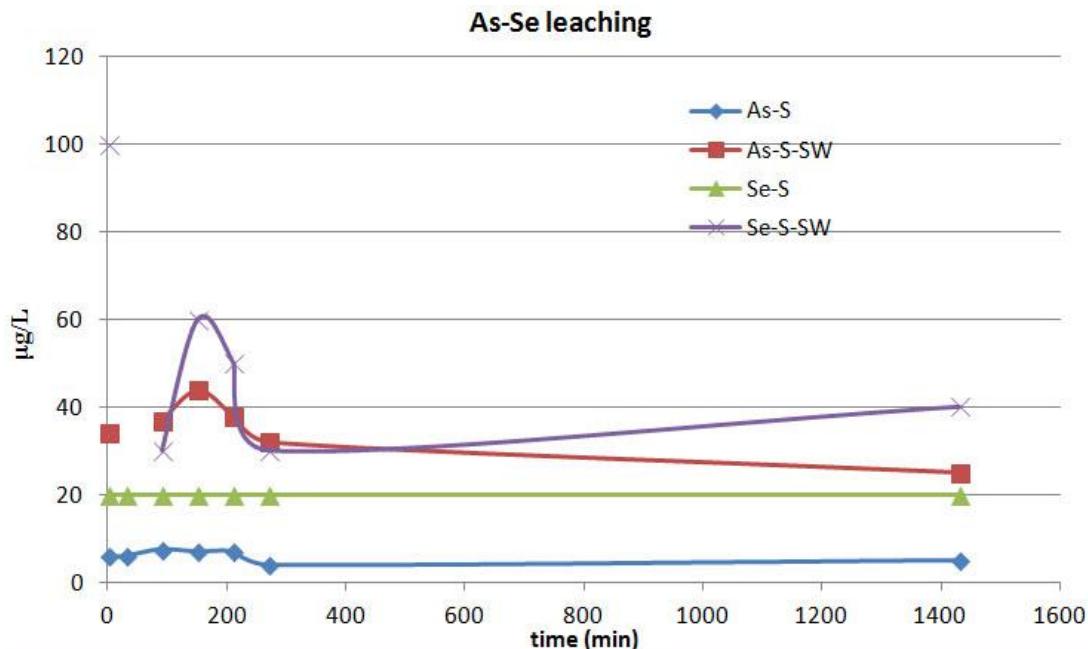


Figure 4. Evolution of As and Se in the pilot-scale experiments. Values in $\mu\text{g/L}$. As/Se-S: change of As and Se content in time, measured in effluent solution of not-amended experiment, As/Se-S-SW: change of As and Se content in time, measured in effluent solution of amended experiment.



3.3. Geochemical Modeling

Hydrogeochemical modeling of the leachates using Minteq showed that the degree of complexation of Cu rose 56.3% and 57.6% in leachates with sewage sludges (Table 6), although Cu was immobilized by biosolids (Figure 2). Moreover, the pH-Eh diagram from the Medusa numerical code [43] showed that CuCl_3^- was the most stable species and $\text{CuCO}_3 \text{ (aq)}$ was the most stable carbonated species. Thus, the immobilization of Cu may be associated with possible sorption by organic matter and adsorption by oxyhydroxides of Fe, since leachates are saturated with respect to these mineral phases (Table 7). In addition, Cu may be precipitated as Cu_2S at pH values between 6 and 8 when the Eh is low (0.0 to -125 mV), which was the case in the pilot-scale experiment with amended material.

The partial retention of Pb coincides with the possible precipitation of chloropyromorphite. This was the most stable mineral phase in the pH-Eh conditions of the leachates with amended material, which were saturated with respect to this mineral (Table 7). Leachates were also saturated or slightly undersaturated with respect to cerussite (Table 7). Therefore, this mineral may also control the mobility of Pb. Likewise, Pb showed a high degree of complexation in sewage sludge leachates (67.6%–70.4%, Table 6), although this phenomenon did not seem to increase the mobility of Pb.

Table 6. Distribution of species in leachates of soils and slags (E-1, E-7) and leachates of amended materials (LE-1, LE-7) in the pilot-scale experiments.

Species	E-1(%)	E-7(%)	LE-1(%)	LE-7(%)
Cu ⁺²	3.01	2.79	5.07	4.14
Cu DOM1	0.14	0.17	56.36	57.63
CuOH ⁺	2.31	7.52	1.69	1.29
Cu(OH) ₂ (aq)	0.16	1.66	0.05	0.04
CuCl ⁺	0.07	0.01	0.70	0.53
CuSO ₄ (aq)	1.30	1.33	2.21	2.22
CuHPO ₄ (aq)	0.09	0.12	0.22	0.22
CuCO ₃ (aq)	85.25	81.50	31.80	31.81
CuHCO ₃ ⁺	0.52	0.15	0.40	0.42
Cu(CO ₃) ₂ ⁻²	7.10	4.62	1.33	1.59
Pb ⁺²	4.36	4.36	3.05	2.53
Pb DOM1	0.42	0.54	67.68	70.43
PbOH ⁺	2.65	9.32	0.81	0.63
Pb(OH) ₂ (aq)	0.03	0.35	-	-
PbCl ⁺	2.03	0.52	7.76	5.91
PbCl ₂ (aq)	0.08	-	2.04	1.43
PbSO ₄ (aq)	4.02	4.43	2.84	2.91
Pb(SO ₄) ₂ ⁻²	0.29	0.23	0.48	0.58
PbNO ₃ ⁺	0.03	-	0.24	0.13
PbHPO ₄ (aq)	0.01	0.01	0.01	0.01
Pb(CO ₃) ₂ ⁻²	5.64	3.96	0.44	0.53
PbCO ₃ (aq)	70.89	73.1	11.01	11.21
PbHCO ₃ ⁺	9.49	3.06	3.06	3.30
Sb(OH) ₃	99.99	99.97	99.99	99.99
Mn ⁺²	60.57	60.63	65.74	62.12
MnOH ⁺	0.03	0.13	0.01	0.01
MnCl ₂ (aq)	0.02	-	0.98	0.78
MnCl ⁺	0.77	0.20	4.60	3.99
MnSO ₄ (aq)	20.29	22.37	22.24	25.89
MnNO ₃ ⁺	0.04	-	0.56	0.35
MnHPO ₄ (aq)	0.37	0.54	0.59	0.67
MnHCO ₃ ⁺	3.30	1.06	1.65	2.02
MnCO ₃ (aq)	14.56	15.03	3.50	4.06
Ni ⁺²	52.51	57.99	52.68	47.47
Ni DOM1	0.06	0.09	14.69	16.59
NiOH ⁺	0.16	0.62	0.07	0.05
NiCl ⁺	0.25	0.07	1.37	1.13
NiSO ₄ (aq)	19.74	24.00	20.00	20.20
NiNO ³⁺	0.06	0.01	0.71	0.43
NiHPO ₄ (aq)	0.11	0.17	0.16	0.17
NiCO ₃ (aq)	9.36	10.6	2.08	2.3
NiHCO ₃ ⁺	17.71	6.29	8.17	9.58

Table 7. Calculated saturation index for selected leachates of pilot-scale experiments. Saturation indices calculated using MINTEQ.

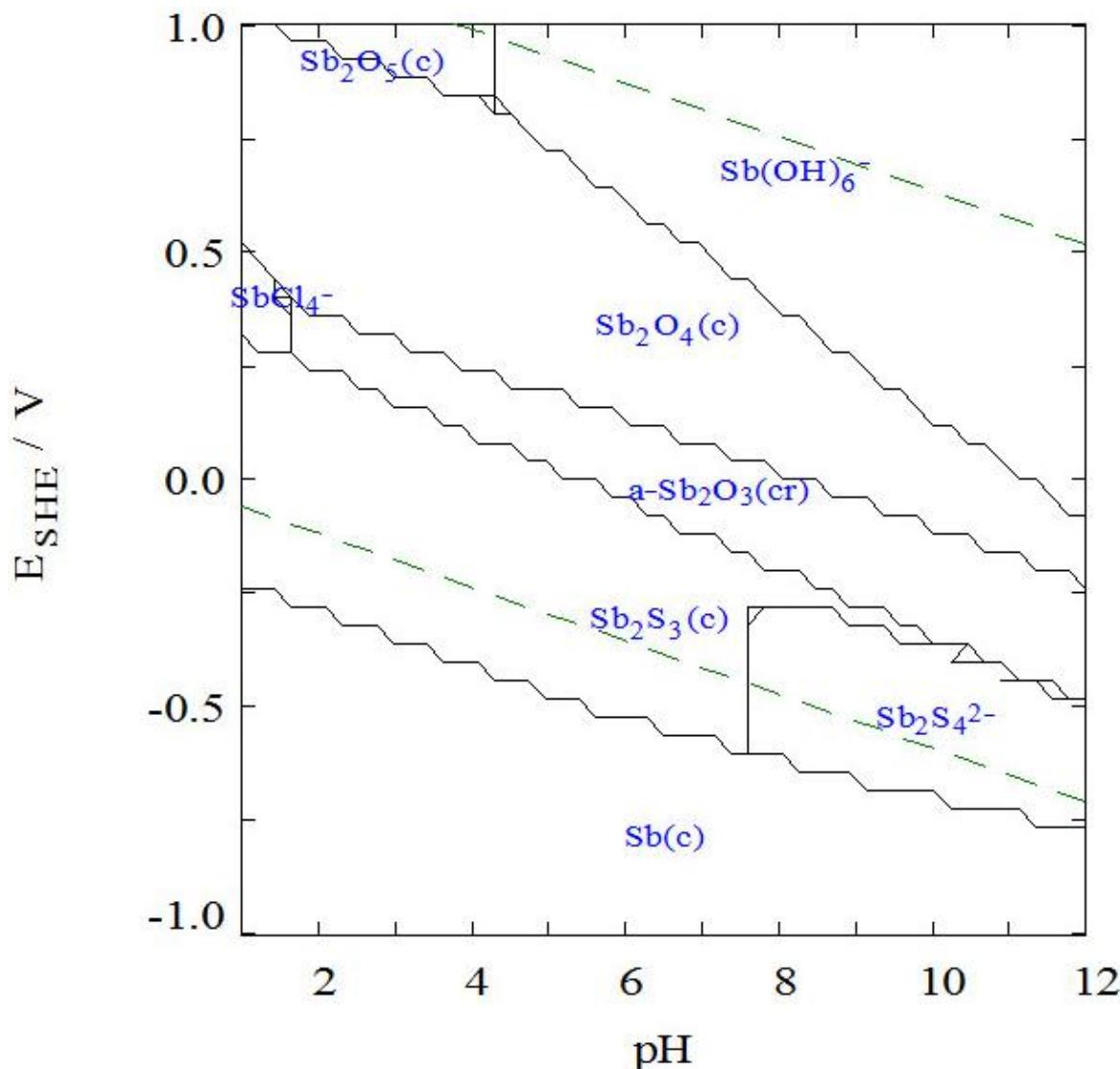
Phase Mineral	Leachate E-1	Leachate E-7	Leachate LE-1
<i>Fe oxy-hydroxides</i>			
Fe(OH) ₃	5.874	6.281	5.621
Goethite	8.073	8.48	8.12
Fe(OH) _{2.7} Cl _{0.3}	8.822	8.889	9.098
<i>Sulfates</i>			
Jarosite	5.805	4.869	8.055
Jarosite-Na	1.73	0.701	3.836
Gypsum	-0.346	-0.371	-0.042
<i>Pb minerals</i>			
Cerrusite	0.115	-0.477	-0.965
Chloropyromorphite	12.217	10.647	10.307
<i>Cu minerals</i>			
Cu(OH) ₂	-2.253	-0.792	-2.773
Azurite	-2.036	0.272	-3.547

The retention of Sb may be associated with possible precipitation of Sb₂O₃, which was the most stable mineral phase in the experimental conditions (Figure 5). The mobility of metalloids such as As and Se is favored by the pH-Eh conditions of leachates, since under elevated pH the anionic forms of As may be desorbed from solid phases and As becomes relatively mobile under reducing conditions. Thus, in the leaching of lead metallurgical slags in high-molecular-weight organic solutions, metals and As are released in large amounts during the early stage of the experiments [5]. In addition, organic acids from biosolids may reductively dissolve the Fe oxyhydroxides associated with weathered slags and mobilize Fe, Ni, Cu, Cr and Co by reductive dissolution, as shown in similar situations [25].

In the pH-Eh conditions of the column experiments, the most stable Ni species is NiCl₂ under oxidizing conditions. The precipitation of NiO₂ is only possible under oxidizing conditions at high pH values (>8.5). At a low redox potential, a high pH could cause precipitation of the sulfide NiS. Thus, Ni mobilization in the experiments may be caused by the presence of significant amounts of leachable Ni in the sewage sludge (39 mg/kg) and the high Cl⁻ content, although the complexation of Ni with dissolved organic matter is significant (Table 6). In addition, similar experiments suggested the migration of Ni as organic complexes [29].

The mobility of Mn is probably derived from the dissolution of olivine, which may contain up to 3.35% of MnO [9]. The dominant aqueous species in leachates are Mn²⁺ (60%–65.7%) and MnSO₄ (20.2%–25.8%, Table 6), which coincides with the pH-Eh diagram.

Figure 5. Eh-pH diagram for the system Sb-SO₄-H₂O. Built by MEDUSA code (Puigdomènech 2004). (c): solid phase; E_{SHE/V}: Eh (volts); [Cl⁻]_{TOT} = 32.72 M; [Sb(OH)₃]_{TOT} = 10.00 mM; [SO₄²⁻]_{TOT} = 16.14 M; T = 25 °C.



4. Conclusions

The leaching experiments with organic amendments on contaminated soils and smelter slags showed that As, Se, Ni and Mn were mobilized, whilst Cu, Pb and Sb were retained. The removed metals: Cu, Pb and Sb, decreased their concentrations from 250 µg/L, 80 µg/L and 6 µg/L, respectively in the leachates of contaminated materials, to <20 µg/L, 40 µg/L and 4 µg/L, respectively, in the amended material. The immobilization of Cu by sewage sludge may be associated with possible sorption by organic matter and adsorption by oxyhydroxides of Fe, as leachates are saturated with respect to these mineral phases. In addition, Cu may be precipitated as Cu₂S at pH values between 6 and 8 when the Eh is low (0.0 to -125 mV), which is the case in the slag/sewage sludge experiment. Although lead mobility is favored by high dissolved organic carbon concentrations, the possible precipitation of chloropyromorphite may control the mobility of Pb in the leaching experiments. As and Se were leached in the sewage sludge experiment, which indicates that high pH and reducing

conditions may mobilize these metalloids. The leaching experiments indicated that the formation of organo-Ni complexes in sludge-amended slags might be an important factor in Ni leaching. The organic amendments used in this study increased some metal and metalloid concentrations in the leachates (As, Se, Fe, Mn and Ni). This suggests that the amendments could promote groundwater and seawater contamination in the Sierra Almagrera coastal region, if they are used to remediate slag-contaminated areas. However, organic amendments did not increase Cu, Pb and Sb concentrations. Hence, they may be used as reactive material in contaminated areas, if these metals are the priority contaminants of smelting sites. Furthermore, the high salinity associated with sewage sludges may favor metal mobility due to the increase in ionic strength and the possible cation exchange associated with the high Na and K content of sewage sludges.

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