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Effects of sewage sludge application on heavy metal leaching from mine tailings impoundments

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Abstract

Column experiments were conducted to investigate the removal of heavy metals from two mine tailings (El Arteal and Jaravías) using sewage sludge as a reactive material. When sewage sludge is used as a reactive material on the El Arteal tailings (sample SA), Fe, Mn, Zn and Pb are removed and Cu and Ni are mobilized. The experiments carried out on the Jaravías tailings give similar results, showing the retention of Cu, Pb, Fe and Mn and the mobilization of Ni and Zn. An analysis performed using the PHREEQC numerical code suggests that the retention of Fe in the sewage sludge may be caused by the precipitation of $Fe(OH)_{2.7}Cl_{0.3}$ and possibly pyrite, and that the retention of Pb at high pH may be caused by the formation of stable phase minerals such as $Pb(OH)_2$ and PbS in these conditions. Ni mobilization in the column experiments with the two tailings samples may be caused by the presence of significant amounts of leachable Ni in the sewage sludge. The complexation of metals with dissolved organic matter, calculated with the Minteq model, may be moderate.

Keywords: Sewage sludge; Contamination; Metals; Mine tailings; Remediation

1. Introduction

Many authors have studied the contamination problems associated with the presence of metals in soils and aquifers caused by mining activities in various locations (Förstner and Wittman, 1979; EPA, 1996; McGregor et al., 1998; Blowes and Jambor, 1990; Blowes and Ptacek, 1994; Dold and Fontboté, 2001; Al et al., 2000; Blowes et al., 2004; Lottermoser, 2003; Jambor et al., 2003; Navarro et al., 2006a; Romero et al., 2007). The type of contaminants and their concentration in the environment depend on their initial concentrations and, in mining areas, on the nature of the mineral deposit in question (Seal et al., 2002). The presence of As, Fe, Cu, Zn, Cd, Co, Ni, Pb, Hg, Tl, Se, Te and Sb is very common. Thus, when mine waste (waste rock dumps, tailings and slags, mainly) are disposed of without any environmental control, mining activities may cause greater soil and groundwater contamination.

The use of sewage sludge on waste rock dumps is based on supplying nutrients to promote plant growth (Theodoratus et al., 2000; Simon, 2005) in order to improve biomass production (Pichtel et al., 1994) and evaluate the availability of metals after the application of sludge to tailings deposits (Forsberg and Ledin, 2006). Organic amendments such as biosolids can contribute to the rehabilitation of mineral sand mines and do not constitute a heavy-metal contamination threat to soils or plants (Rate et al., 2004).

Besides supplying nutrients to plants, sludge may promote immobilization and the uptake of some metals by plants, although some studies have shown an increase in sulfide oxidation or reductive dissolution reactions in mine waste (Ribet et al., 1995; Cravotta, 1998) and the release of metals.

Thus, the use of manure compost and sewage sludge on Pb/Zn tailings have shown a decrease in pH, an increase in electrical conductivity (EC) and in extractable Cu, and

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a decrease in extractable Pb and Zn (Chiu et al., 2006). Furthermore, Ni may migrate as organic complexes when sewage sludge is applied to soil. This is potentially environmentally significant, due to the relatively poor retention of Ni by the sludge (Ashworth and Alloway, 2004). 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 (Schwab et al., 2007).

Laboratory studies with composted sludge have shown that this material has a high affinity for heavy metals such as Pb, with a retention capacity of 15 wt% (Urasa and Macha, 1997). Basta et al. (2001) investigated the effectiveness of lime-stabilized biosolids at reducing the extractability and bioavailability of Cd, Pb and Zn from smelter-contaminated soils, and showed that alkaline organic treatments reduced metal extractability and phytoavailability. Also, the use of municipal sewage sludge compost with $CaCO_3$ and red fescue (*Festuca rubra*) can stabilize metals in acidic and phytotoxic mine spoils (Simon, 2005).

In the treatment of acid mine drainage, laboratory column experiments have proven useful for simulating the effect of biosolids on the reduction of contaminant mobilization. Santibáñez et al. (2006) showed the reduction of EC value and NO_3 concentration in a percolate of biosolids mixed with tailings. Waybrant et al. (2002) demonstrated a reduction in Fe (1200–300 to <0.01 mg/L), Zn (0.06–0.01 mg/L), Ni (0.8–12.8 to <0.01 mg/L) and sulfates in pyrite wastes amended with a mixture of wood chips, sawdust, composted municipal sewage sludge and leaf compost.

Similar column experiments, based on a mixture of municipal compost and calcite percolated by mine water simulating the contaminated groundwater resulting from the Aznalcóllar mine tailings dam failure, showed the removal of Fe, Al, Zn and Cu. The metal removal was attributed to the precipitation, co-precipitation and sorption of metal oxyhydroxides and carbonates onto the biosolid surface (Gibert et al., 2005). The use of biosolids composed of woodchips and pulp waste as a reactive layer has shown a decrease in sulfates, Fe and Zn in water in tailings impoundments (Hulshof et al., 2006).

When biosolids are used as reactive layers or permeable reactive barriers (PRBs), the redox reactions catalyzed by biological processes may remove many inorganic cations or inorganic anions by means of the indirect precipitation resulting from the oxidation or reduction of inorganic cations. Thus, Ag, Cd, Co, Cu, Fe, Ni, Pb and Zn are removed by the precipitation/coprecipitation of these metals as sulfides (EPA, 1998; Ludwig et al., 2002; Bolzicco et al., 2001; Blowes et al., 2000, 2004; McGovern et al., 2002; Naftt et al., 2002; Navarro et al., 2006b; Vidic et al., 1996).

In one current treatment technique, an organic carbon reactive material is used to stimulate sulfate reduction and the subsequent metal sulfide precipitation (Amos et al., 2004). The H_2S generated in the sulfate reduction, the Fe (II), and other metallic species such as As, Cd, Co, Cu, Ni, Pb and Zn may precipitate, thereby producing sulfide minerals.

This study aims to characterize sewage sludge for use as a reactive material, evaluate the sludge's effect on the removal of metals in two tailings deposits of the old Sierra Almagrera mining district (Almería, Spain), and model the main hydrogeochemical processes related to the contaminants in the reactive material.

2. Methods

2.1. Site description

In SE Spain, especially in the provinces of Murcia and Almería, there are many ore deposits (mainly of base metal sulfides) that were mined in the 19th and 20th centuries (Navarro et al., 1998, 2000, 2004, 2006a; Viladevall et al., 1999). This long-term mining activity resulted in the dumping of very large amounts of mine waste, including waste rock, tailings and smelting slags, all along the coastal area of the SE Iberian Peninsula. At present (2007), the pressure of urban and agricultural development in this area has led to the occupation of land and soils contaminated by mine waste. This involves environmental risks associated with the inhalation of pollutants, the contamination of surface water and groundwater, and the migration of contaminants to plants.

The study area has a semi-arid climate with an average annual precipitation of 200 mm. Using mean annual balances, approximately 90% of the precipitation is converted into evapotranspiration. Surface runoff is very significant, since 50% of the annual precipitation can fall in 1–2 days. Therefore, the main primary-source contaminant mobilization mechanisms are runoff and infiltration together with the mechanical dispersion caused by the wind. Groundwater pollution and soil fertility loss are the main types of environmental degradation brought about by the uncontrolled disposal of mining waste in this area (Navarro et al., 2004).

The Sierra Almagrera mining district is located along the eastern border of the Betic Cordillera, which is the central part of a wide volcano-tectonic and metallogenic belt extending from Cabo de Gata to Sierra de Cartagena. In the study area, the Almanzora river basin (1800 km^2) overlies a tectonic basin between two metamorphic ranges: Sierra Almagrera and Sierra de Almagro. It is filled with Tertiary deposits and covered with Quaternary alluvial and deltaic deposits from the Almanzora River. The two main tailings deposits of Sierra Almagrera extend into a non-confined aquifer formed by the alluvial and deltaic deposits of the Almanzora River (El Arteal deposit) and into the metamorphic basement (Jaravías deposit).

In the study area, the main environmental concern associated with past mining activities is the uncontrolled accumulation of tailings in two main waste deposits, El Arteal (3,500,000 t) and Jaravías (300,000 t), which pose a high environmental risk. In fact, the dispersion of contaminants has affected nearby agricultural and urban soils (Navarro et al., 2004, 2006a), and the smelting slag dumping sites have affected the groundwater and stream sediments of the main drainage network.

2.2. Sampling and analysis of tailings

Tailings and stockpiles were disposed near the old mining facilities. At present, they occupy an agriculturally intensive area. Solid materials were collected between 1996 and 2006 by driving a small-diameter pipe vertically into the ground, using a methodology derived from standardized methods for describing and sampling contaminated soils (USEPA, 1991) and by hand excavation to a depth of 0.4 m.

After drying at 30 °C for 48 h, solid samples were sealed to minimize exposure to atmospheric gases. After the samples were homogenized, the grain size, porosity, bulk density, pH and EC were determined. Homogenized tailings samples were ground in a mechanical mortar in order to perform chemical analyses (Fritsch Pulverisette 502).

The total amount of metals and trace elements was found 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.

The mineralogy of the mine wastes was examined under a binocular microscope and was analyzed using X-ray powder diffraction (XRD) at Actlabs (Ontario, Canada). Phase identification was accomplished by comparing the diffraction patterns with a library of over 17,000 mineral patterns stored in the International Centre for Diffraction Data (ICDD).

2.3. Leaching tests

To evaluate the mobility of contaminants, column experiments were performed under controlled laboratory conditions. The column was made in a methacrylate cylinder, which allowed visual examination of the progress of the wetting front and the detection of preferential flow channels along the column walls. The column was 750 mm long, had an outer diameter of 150 mm and was 5 mm thick. The column's dimensions minimized the occurrence of channeling, generally the main problem of column experiments, by making the column diameter at least 30 times the maximum particle size found in the material (Relyea, 1982). In the study the equivalent diameter of solid particles ranges 2–20 μm in the sewage sludge and 0.02 mm in the tailings, therefore the column diameter is sufficient greater than the particles size.

The longitudinal column's dimension, in the experiments with sewage sludge and mine tailings, is occupied by 0.1 m of mine waste in the upper zone and 0.2 m of sludge below, comprising a sufficient volume of porous media. Attached to the lower part of the column was a plastic funnel with a length of 222 mm and an inner diameter of 186 mm. A perforated fiberglass plate was installed inside the funnel to support the column's methacrylate structure. The plate was covered by a mesh filter that retained the porous medium. The entire device was mounted on top of a metal structure that allowed the height above the surface and the verticality of the column to be regulated.

Low mineralized water entered the column through an injection system connected to a ProMinent® Beta® BT4a metering pump, which emitted a maximum flow of 10 L per hour and could be adjusted from 1% to 100%. A constant-head reservoir was used to deliver influent water at a flow rate of 0.027 L min^{-1}, which represented, approximately, the recharge flow rate at the aquifer. The inflow fluid is low mineralization water, which approximates the behaviour of rain water over the tailings in environmental conditions. The samples were collected at the bottom of the column as a function of time. The first sample, corresponding to time 0, was taken when water started to flow from the lower part of the column. Flow, pH and EC were measured immediately after sample collection.

In order to evaluate the factors that control the mass-transfer in the column experiments and the proximity to equilibrium conditions, although this condition may be obviated (Wehrer and Totsche, 2003, 2005), was calculated the Damköhler number. Thus, the Damköhler number expresses the rate of reaction relative to the advection or fluid flow rate, so that when Damköhler numbers exceeding 10 indicate near equilibrium conditions (Wehrer and Totsche, 2005). The Damköhler number is expressed by:

$$D_a = R \cdot K \cdot L \cdot V^{-1}$$

where K is the mass-transfer rate, R is the coefficient of retardation, L the length characteristic of fluid domain (column length) and V the pore velocity. In the column experiments performed, the pore velocity is, approximately, 3.73×10^{-3} m/min, and the kinetic constant K ranges between 0.01 and 0.02, which was obtained from the fitting of elution curves to an exponential mathematical expression. Using retardation factors comprised between 2 and 5, the Damköhler number of the column experiments reaches values of 6.1, indicating a situation close to equilibrium conditions. In addition, the number of pore volumes reached in the column experiments is:

$$T_a = V \cdot t \cdot L^{-1}$$

where T_a is the number of pore volumes and t is the time of lixiviation. The final T_a is 6.8 pore volumes, indicating a time period which may be considered as representative.

The pH, redox potential (Eh; mV), temperature and EC (μS/cm), corrected using standard solutions, were measured *in situ* with portable devices (HACH sensION TM378). The samples were filtered with 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 HNO_3. The samples were collected in 110 ml high-density polypropylene bottles, sealed with a double cap and stored in a refrigerator until analysis.

The major cation concentrations were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the minor cation concentrations were measured using inductively coupled plasma mass spectroscopy (ICP-MS) and ICP-OES at the laboratories of the University of Barcelona and ACTLABS. The standard reference material NIST 1640 (ICP-MS) was used to evaluate accuracy.

Hydrogeochemical analyses of leachates were performed using the PHREEQC numerical code (version 2.10.03) (Parkhurst et al., 1999) to evaluate the speciation of dissolved constituents and calculate the saturation state of the effluents. The Minteq thermodynamic database was used for the chemical equilibrium calculations. The total concentrations of Fe, Mn and other elements were used in the geochemical modeling.

3. Results and discussion

3.1. Chemical and physical characteristics of tailings and biosolids

Mine tailings were collected from two waste impoundments located in the Sierra Almagrera mining district: the El Arteal deposit (SA) and the Jaravías deposit (JAR). The chemical analyses of the El Arteal tailings samples (Table 1) show high concentrations of Ag (mean: 26.6 ppm), As (mean: 278.4 ppm), Ba (mean: 58,000 ppm), Cu (mean: 59 ppm), Pb (mean: 2879.3 ppm), Sb (mean: 169.8 ppm) and Zn (2179.2 ppm). In the Jaravías deposit, the chemical composition of the tailings shows a large amount of Ba (2.8%) and high contents of Ag (15.8 ppm), As (302.2 ppm), Cr (28.5 ppm), Pb (1830 ppm), Sb (69.1 ppm) and Zn (1557.5 ppm).

The mineralogy of the tailings was examined under a binocular microscope, and by X-ray powder diffraction (XRPD) for the fine fraction. The results of the mineralogical study indicate that the most abundant primary phases are galena (PbS), pyrite-marcasite (FeS_2), siderite ($FeCO_3$), barite-celestite ($BaSO_4$–$SrSO_4$), quartz (SiO_2), calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$) and clay minerals. The least-soluble secondary minerals are jarosite ($KFe_3(SO_4)_2(OH)_6$), natrojarosite ($NaFe_3(SO_4)_2(OH)_6$), crystalline oxyhydroxide of Fe (goethite), amorphous ferric hydroxide ($Fe(OH)_3$), clay minerals, anglesite ($PbSO_4$), alunite ($KAl_3(SO_4)_2(OH)_6$) and gypsum ($CaSO_4 \cdot 2H_2O$). Other secondary minority phases are plumbojarosite ($PbFe_6(SO_4)_4(OH)_{12}$), langite ($Cu_4(SO_4)(OH)_6 \cdot 2H_2O$), uklonskovite ($NaMg(SO_4)F \cdot 2H_2O$), ferrohexahydrite ($FeSO_4 \cdot 6H_2O$) and szomolnokite ($FeSO_4 \cdot H_2O$).

The air-dried mine tailings were passed through an analytical sieve shaker (RETSCH AS 200). This indicated a dominant granulometric fraction of fine sand-silt due to the milling process before flotation. The pH values measured at the tailings range from 2.90 to 6.90. A low hydraulic conductivity of approximately 0.049 m/d was calculated using a perameter of constant head in the laboratory. The result is a highly contaminated area with large amounts of Ba and significant contents of Ag, As, Pb, Sb and Zn, which exceed the values of the Netherlands Soil Contamination Guidelines.

The sewage sludge used in the laboratory experiments, produced at the DSM-Deretil industrial facilities in Villaricos (Cuevas del Almanzora, Almería), is a stabilized biosolid with a pH between 7.79 and 8.40, a moisture content of 52.7%, an electrical conductivity comprised between 34.8 and 43.5 mS/cm and a grain size silty (2–20 μm). The chemical composition of the sludge shows a high content of Ca (29.9%), K (0.25%), Mg (0.94%), and Na (2.25%), possibly due to the use of seawater in the treatment process that created the sludge. The metal content in the sludge is low, and the amounts of As (3.2 ppm), Ba (<50 ppm), Cd (<0.5 ppm), Cr (21 ppm), Cu (7 ppm), Fe (0.16%), Hg (<1 ppm), Mn (67 ppm), Ni (17 ppm), Pb (<5 ppm) and Sb (1.2 ppm) are below the concentrations detected in the non-contaminated soils of the region (Table 1). However, Zn concentrations (127 ppm) are above

Table 1
Mean chemical composition of tailings and samples used in the leaching tests

	Ag	As	Ba	Cd	Cr	Cu	Hg	Fe	Pb	Se	Sb	Sr	Zn
El Arteal tailings													
Mean	26.6	278.4	5.8	17.6	80.6	59.0	–	12.43	2879.3	–	169.8	0.53	2179.2
Min	5.0	200	3.2	5.8	52.0	21.0	<1	10.0	1588.0	<3	66.0	0.28	1520.0
Max	46.0	460	10.0	35.0	130	134.0	3.0	15.4	5428.0	<5	270.0	1.0	3000.0
Sample SA	27.5	265	4.9	5.8	84.5	27.5	<1	13.1	1881	<3	190	0.45	2220
Jaravías tailings													
Mean	15.8	302.2	2.8	4.6	28.5	22	<1	22.2	1830	–	69.1	1.1	1557.5
Min	10.4	62.8	2.2	4.6	20	22	<1	20	1830	<3	44.5	0.75	1170
Max	23	960	3.6	4.6	39	22	<1	23.8	1830	<5	100	1.7	2000.0
Sample JAR	10.4	62.8	2.5	4.6	20	22	<1	20.0	1830	<3	44.5	0.75	1660
NCS	<0.3	12.2	0.024	0.06	–	12	<1	3.59	12	<3	2.8	0.01	81
NH(*)	15^{**}	55	0.0625	12	380	190	10	–	530	100^{**}	15	–	720

SA: El Arteal deposit, JAR: Jaravías deposit. Values in ppm, except Ba (%), Sr (%) and Fe (%). NCS: non-contaminated soil, NH(*): Netherlands Soil Contamination Guidelines values, new C-values and (*): serious contamination level.

81 ppm, the value detected in the non-contaminated soils. The metal content of the sludge does not exceed the limits imposed by Spanish environmental regulations (RD 13-10/1990) for total metal content in sewage sludge used on agricultural land.

3.2. Leaching of mine waste

Five laboratory column experiments were performed to evaluate the application of sewage sludge on two representative samples of the main tailings deposits of the study area, the El Arteal deposit (SA) and the Jaravías deposit (JAR), whose chemical compositions are shown in Table 1. The column experiments were carried out in three steps. First a leachate of the pure sewage sludge was obtained in order to evaluate the mobilization of metals and other elements from the biosolid (Table 2). Second, a leachate of two "pure" tailings samples (SA and JAR) was obtained without the use of sludge in order to compare a theoretical contaminant leachate with the effect of the reactive material. The last step was the lixiviation of the tailings (SA and JAR samples) and the sludge in order to evaluate the effect of the reactive material, located in the column below the mine waste.

Moreover, the low mineralized water used in the lixiviation tests shows a low concentration of metals and major cations (Table 2). However, the lixiviation test with "pure" sewage sludge showed the possible mobilization of Ni and Zn. Besides, significative amounts of Na and K were detected, because the saline character of the effluent that produced, in the DSM wastewater plant, the sewage sludge used in this study (Table 2).

The results of the use of sewage sludge on the tailings from the El Arteal deposit (sample SA) show that the reactive material removes Zn and Pb, since the concentrations obtained without sludge were 902–207 and 298–42 μg/L, respectively, and the leachate produced with sludge has concentrations of 105–15 and 10.2–4.3 μg/L, respectively (Fig. 1). The leachate produced with sludge shows a significant reduction of Fe and especially Mn, which decreases from 8600–1500 μg/L to 130–25 μg/L (Fig. 2). However, some metals are mobilized, in particular Cu and Ni

Table 2
Chemical composition of sewage sludge lixiviation with low mineralized water (LMW)

Time (min)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Ca (mg/L)	Cr (μg/L)	Mn (μg/L)	Fe (μg/L)	Ni (μg/L)	Cu (μg/L)	Zn (μg/L)	Pb (μg/L)
0	1535	133.1	151	126.3	11	274	604	161	178	<0.5	<0.1
60	64.0	9.67	3.84	18.0	1.5	9.8	7	14	11.4	447	134
120	9.2	5.02	1.15	6.3	1.0	5.4	<0.5	5.5	7.7	<0.5	<0.1
180	2.9	2.99	0.45	6.8	1.9	7.9	69	2.2	3.2	<0.5	<0.1
240	3.2	2.58	0.56	4.6	0.5	3.3	<0.5	1.8	8.0	<0.5	<0.1
300	1.4	1.54	0.26	5.0	<0.5	2.4	<0.5	1.9	1.1	<0.5	<0.1
360	0.99	1.17	0.20	3.0	<0.5	1.4	<0.5	0.5	<0.2	<0.5	<0.1
420	1.43	1.28	0.21	5.5	<0.5	2.8	<0.5	0.7	0.8	<0.5	<0.1
480	1.03	1.13	0.19	3.4	<0.5	1.1	<0.5	0.4	<0.2	<0.5	<0.1
540	0.91	1.04	0.17	3.4	<0.5	1.5	<0.5	0.4	4.9	<0.5	<0.1
LMW	13	4.4	1.1	38.2	<0.5	<0.1	<0.5	<0.3	<0.2	<0.5	0.3

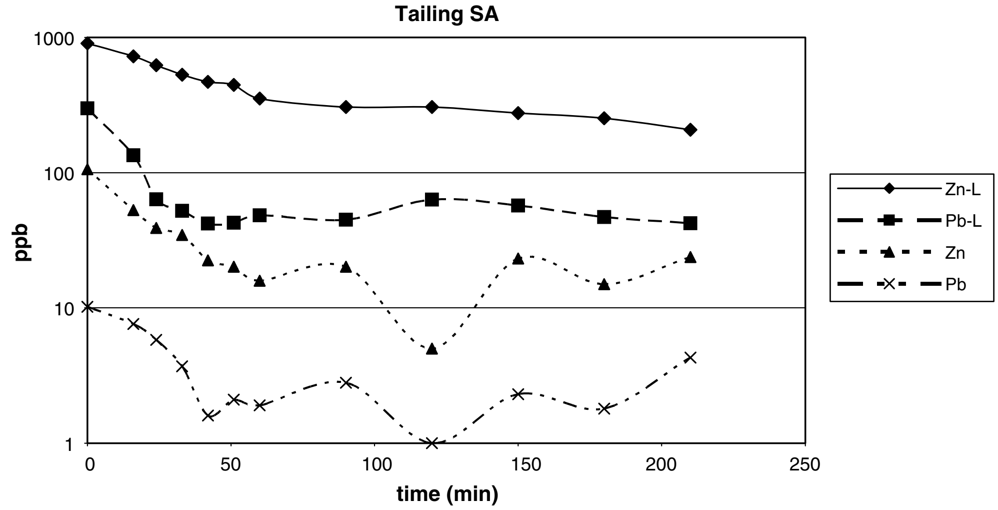

Fig. 1. Changes in Zn and Pb in the lixiviation tests. Zn-L: leaching of pure tailings, Zn: leaching of mine waste with sludge. El Arteal tailings deposit (SA sample).

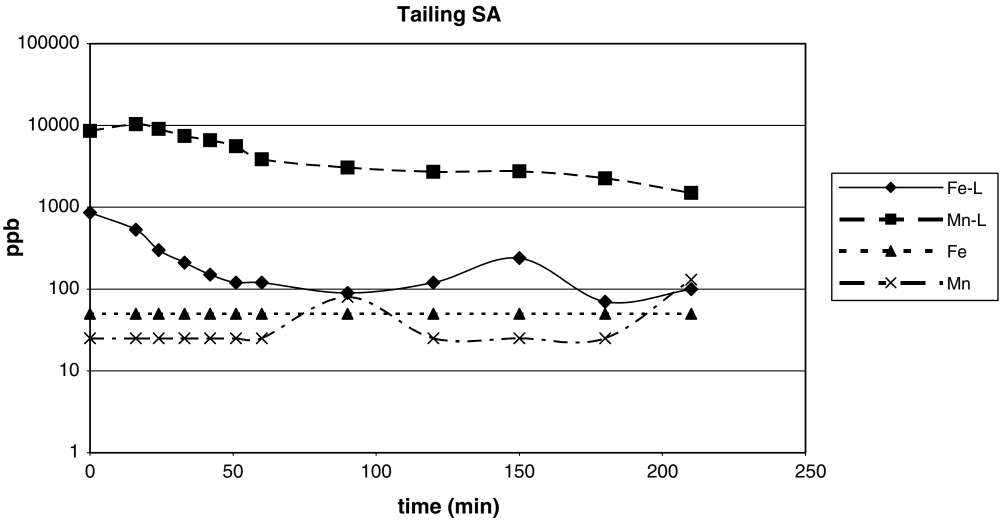

Fig. 2. Changes in Fe and Mn in the lixiviation tests. Fe-L: leaching of pure tailings, Fe: leaching of mine waste with sludge. El Arteal tailings deposit (SA sample).

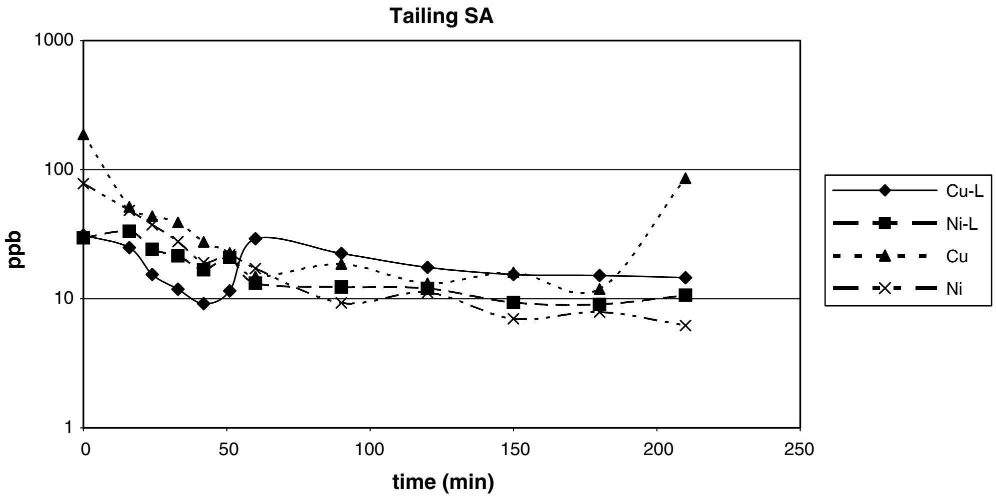

Fig. 3. Changes in Cu and Ni in the lixiviation tests. Cu-L: leaching of pure tailings, Zn: leaching of mine waste with sludge. El Arteal tailings deposit (SA sample).

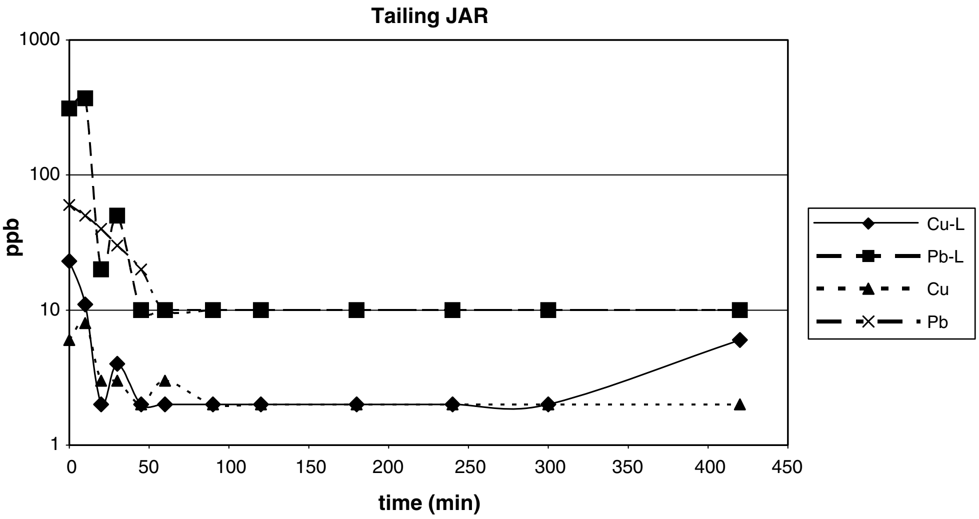

Fig. 4. Changes in Cu and Pb in the lixiviation tests. Cu-L: leaching of pure tailings, Cu: leaching of mine waste with sludge. Jaravías tailings deposit (JAR sample).

(Fig. 3). The mobilization of Cu at the end of the lixiviation test may be produced by the increase of pH, which rises until 9 in this experiment (Fig. 3).

The experiments conducted with the Jaravías tailings show similar behavior, i.e. the retention of Cu, Pb, Fe and Mn (Figs. 4 and 5) and the mobilization of Ni (Fig. 6) in proportions similar to those found in the SA column experiment. Zn is mobilized in the JAR sample (Fig. 6), whereas it was retained in the SA sample. These results are similar to those obtained in other column experiments, which have detected the removal of metals such as Fe, Al, Zn and Cu (Gibert et al., 2005). Furthermore, the results of both lixiviation experiments show the mobilization of Ni at leached-Ni concentrations of 6.2–78.1 μg/L in the SA sample and 7–126 μg/L in the JAR sample. In the case of Cu and Ni (Figs. 4 and 6), at the end of the assay, was detected a little increase, which may be not significative, because their proximity to detection level of these metals.

Ni mobilization has been detected in column experiments (Ashworth and Alloway, 2004) that have suggested the migration of Ni as organic complexes. Likewise, Cu mobilization, like that observed in the leaching experiment with the El Arteal tailings, was found in a study of the addition of organic waste to Pb–Zn tailings (Clemente et al., 2006), possibly due to the increase of Cu solubility through organic matter chelation. The changes in Eh in the leachates were very similar in both sludge experiments. The redox potential was initially positive (50–70 mV) and changed to negative over the course of the experiment. The pH ranged from 7 to 8 in the JAR experiment and from 7 to 9 in the SA experiment.

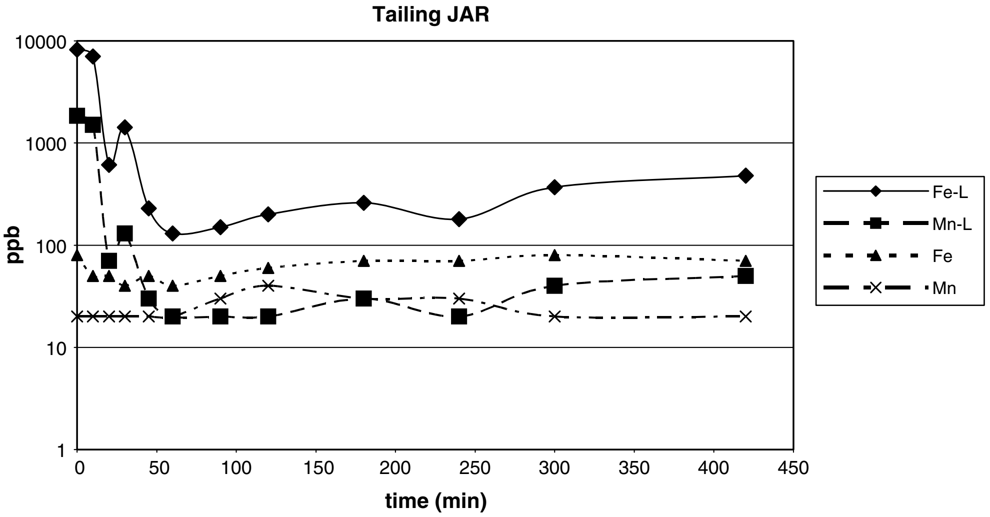

Fig. 5. Changes in Fe and Mn in the lixiviation tests. Fe-L: leaching of pure tailings, Fe: leaching of mine waste with sludge. Jaravías tailings deposit (JAR sample).

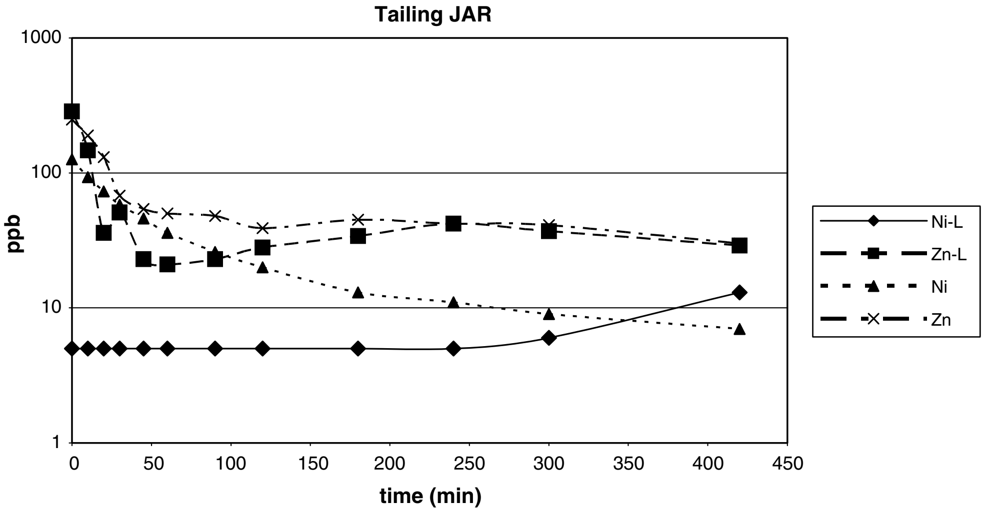

Fig. 6. Changes in Ni and Zn in the lixiviation tests. Ni-L: leaching of pure tailings, Ni: leaching of mine waste with sludge. Jaravías tailings deposit (JAR sample).

4. Hydrogeochemical modeling

Hydrogeochemical analyses of the first leachate samples JA-01 (Jaravías tailings) and MR-01 (Jaravías tailings and sewage sludge) were conducted in order to evaluate the speciation of dissolved constituents and calculate the saturation state of the effluents (Tables 3 and 4). The numerical code PHREEQC (version 2.10.03) was used for these calculations.

The oxidation and subsequent dissolution of sulfide minerals, mainly pyrite and marcasite, is the main source of Fe and SO_4, which are mobilized to pore water and, in the column experiments, are carried away. The eluates may represent the natural pore water formed in the tailings during precipitation.

Table 3
Distribution of species in leachates from the Jaravías tailings (JAR sample)

Species	JA-01	MR-01
Fe		
Fe^{2+}	6.93×10^{-5}	1.17×10^{-6}
$FeSO_4$	6.26×10^{-5}	2.65×10^{-7}
$FeOH^+$	1.33×10^{-6}	1.94×10^{-9}
Pb		
$PbCl^+$	1.72×10^{-8}	1.16×10^{-7}
$PbCO_3$	1.17×10^{-6}	6.83×10^{-8}
$PbSO_4$	1.12×10^{-7}	2.29×10^{-8}
$Pb(CO_3)_2^{-2}$	6.95×10^{-8}	3.79×10^{-10}
$PbOH^+$	4.54×10^{-8}	3.00×10^{-9}
Pb^{2+}	3.92×10^{-8}	2.64×10^{-8}
$PbCl_2$	5.20×10^{-10}	3.32×10^{-8}
Zn		
Zn^{2+}	1.20×10^{-6}	2.14×10^{-6}
$ZnSO_4$	1.43×10^{-6}	6.37×10^{-7}

JA-01: leachate without reactive material, MR-01: leachate with sewage sludge. Data calculated using PHREEQC and the Minteq database. Values in molality.

Table 4
Saturation indices calculated using PHREEQC and the Minteq database

Phase mineral	JA-01	MR-01
Iron oxyhydroxides		
$Fe(OH)_3$	3.29	−2.07
Goethite	7.68	2.33
$Fe(OH)_{2.7}Cl_{0.3}$	8.30	3.55
Sulfate minerals		
Jarosite	9.45	−4.35
Jarosite-Na	6.47	−7.02
Gypsum	0.33	0.44
Melanterite	−3.97	−6.35
Lead minerals		
Anglesite	−1.88	−2.54
Cerrusite	−0.01	−1.22
Zinc minerals		
Goslarite	−6.24	−6.59
Other minerals		
Calcite	0.49	0.07
Siderite	0.66	−2.24

Hydrogeochemical modeling of the leachate using PHREEQC (Table 3) shows that the most abundant Fe species in the leachate of the pure tailings (sample JA-01) and the leachate with sewage sludge (sample MR-01) are Fe^{2+} and $FeSO_4$. Likewise, the saturation index indicates that ferrihydrite, goethite, jarosite and natrojarosite are clearly saturated. The only exception is ferrihydrite in the leachate with sewage sludge, which suggests, only in this case, the possibility of dissolution (Table 4).

Water is slightly saturated with respect to gypsum (Table 4), in both leachates, indicating that the mineral phase may control sulfate solubility. Also, water is saturated with respect to $Fe(OH)_{2.7}Cl_{0.3}$, in both leachates. The predominant secondary Fe phases within the unconfined tailings are goethite, ferrihydrite, jarosite and soluble Fe-sulfates, which occur as interstitial cements. Since leachates are undersaturated, only, with respect to ferrihydrite (leachate MR-01) and melanterite (mineral phase similar to detected ferrohexahydrite), their dissolution, with the oxidation of pyrite, may explain the high Fe concentrations detected in the leachates. The retention of Fe in the sewage sludge may be caused by the precipitation of $Fe(OH)_{2.7}Cl_{0.3}$ and, possibly, pyrite, because these are the most stable phase minerals in the pH-Eh conditions of the column experiment with sewage sludge.

Lead is clearly removed from the leachates (Figs. 1 and 4). In the pH conditions of the column experiments (7.0–8.0), geochemical modeling indicates that the lead speciation (Table 3) may be dominated by $PbCO_3$(aq) and $PbSO_4$ in the leachate without sewage sludge (JA-01) and by $PbCl^+$ and $PbCO_3$(aq) in the leachate with sewage sludge (MR-01). Therefore, lead concentration could be controlled by several of the mineral phases recognized in the mineralogical study, such as anglesite and cerussite ($PbCO_3$), which are undersaturated in the leachate samples (Table 4). The high ionic strength of the sludge samples and high pH together with low Eh may remove, in these conditions, Pb at high pH, due to the formation of stable phase minerals such as $Pb(OH)_2$ and PbS. At low pH, Pb may be mobilized, since it tends to form relatively soluble chloride complexes such as $PbCl^+$ and $PbCl_2$.

The retention of Mn in both experiments and of Cu in the lixiviation of the JAR sample coincides with the possibility of mobilization of these metals in the pH-Eh conditions of the experiments, since the most stable species are Mn^{2+} and $CuCl_2^-$, respectively. The removal of these elements may therefore be caused by adsorption and/or co-precipitation involving the organic matter of sewage sludge. 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 is the case of the JAR samples.

Zinc may be released to leachates by the oxidation and dissolution of sphalerite, and by the dissolution of secondary phases such as goslarite and smithsonite, which have been detected in Sierra Almagrera (Navarro et al., 2004).

Table 5
Percentage of species for the main metals detected in the leachate MR-01

Species	MR-01 (DOC: 10 mg/L)	MR-01 (DOC: 40 mg/L)
Cu		
Cu^{2+}	28.6	25.0
CuDOM1	4.7	16.7
$CuOH^{+}$	5.3	4.6
Ni		
Ni^{2+}	63.0	62.5
NiDOM1	0.2	1.0
$NiCl^{+}$	2.7	2.7
$NiSO_4$	29.2	29.0
$NiHCO_3$	3.5	3.5
Pb		
Pb^{2+}	9.1	8.3
PbDOM1	3.0	11.1
$PbCl^{+}$	39.1	35.8
$PbCl_2$	16.8	15.3
$PbSO_4$	10.3	9.5
Fe		
$Fe(OH)_2^{+}$	99.0	99.0
$Fe(OH)_3$	0.5	0.5
Zn		
Zn^{2+}	46.0	45.6
ZnDOM1	0.3	1.2
$ZnCl^{+}$	15.7	15.5
$ZnSO_4$	23.4	23.2

DOM: dissolved organic matter.

The retention of Zn in the experiment with the SA sample may be associated with the high pH detected in some leachates, which may cause the precipitation of $Zn(OH)_2$. The mobilization of Zn in the JAR sample experiment may be caused by the pH-Eh conditions. $Zn(SO_4)_4^{6-}$, which is the most stable aqueous phase species in these conditions, is found to be present.

Ni mobilization in the column experiments with the two tailings deposits (Figs. 3 and 6) may be caused by the presence of significant amounts of leachable Ni in the sewage sludge (Table 2). In the pH-Eh conditions of the column experiments, the most stable Ni species is Ni^{2+}, under oxidizing conditions. The precipitation of $Ni(OH)_2$ is only possible under oxidant conditions at high pH values (>8.5). At a low redox potential, a high pH could cause the precipitation of the sulfide NiS.

In order to evaluate the potential role of organic matter in mobility of metals, was used the numerical code Visual Minteq (Allison et al., 1991). 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 (Christensen et al., 1999). Table 5 contains the results of the complex formation of main metals in the first leachate of the Jaravías tailings and sewage sludge (sample MR-01), using a DOC concentration of 10 and 40 mg/L. Table 5 shows that in the leachate sample MR-01, only Cu and Pb show a degree of complexation significative. The degree of complexation for Cu rises 16.7% and 11.1% for Pb, at greater concentration of DOC (40 mg/L). Therefore, in the leachate conditions, the complexation of metals with dissolved organic matter may be moderate.

5. Conclusions

Sewage sludge used in this study affected heavy metal leaching from the two mine tailings considered. In the case of the El Arteal tailings (sample SA) the biosolid removed Fe, Mn, Pb and Zn and mobilized Cu and Ni. The application of sewage sludge on the Jaravías tailings (sample JAR) removed Cu, Fe, Mn and Zn and mobilized Ni and Zn. The mobilization of Ni in the two tailing samples may be caused by the presence of significant amounts of leachable Ni in the biosolid (0.4–161 μg/L). In the leachate conditions, the complexation of metals with dissolved organic matter may be moderate.

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