Soluble minerals in soils affected by sulphur mining in semiarid conditions. Case study of El Arteal (Cuevas de Almanzora, Almería, Spain).

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Résumé

L'activité minière dans le quartier minier de Sierra Almagrera-Las Herrerías a produit de grands volumes de résidus (terrils, boues de flottement, scories de fonte...) On remarque pour sa grandeur la masse de boues de flottement de El Arteal (plus d'un million de m^3) avec une conteneur moyenne élevée en Pb (5428 ppm), As (265 ppm), Zn (2200 ppm), Ba (4,9%), Ag (27,5 ppm), etc. On a étudié la solution (extrait de saturation) de quatre sols proches de ces boues: ils présentent des concentrations très élevées de sulfates et des chlorures, avec des quantités importantes de Fe et Sr et, dans de plus petites proportions, de Pb, Cu, Ni, As, Ba y Cr.

Introduction

Exposure of pyrite (FeS_2) and other sulfide minerals to atmospheric oxygen and moisture results in onset of known weathering reactions (Appelo & Postma 1996). The consequence can be the presence of high amounts of As, Cd, Cu, Co, Cr, Fe, Mo, Ni, Pb, Sb, Zn and other minor elements (EPA 1996) in the soil and/or ground water, as a result of sulfide oxidation.

This paper describes the environmental impact on a semi-arid region of unconfined tailings impoundments caused by recent mining activities in the Sierra Almagrera (SA) district, and so reflects the significance of obsolescent mining areas as a factor in soil and sediment contamination.

The SA mining district is located 90 km from Almeria, the provincial capital of Almeria province, Spain, at the eastern edge of the Cordillera Bética, which forms the central part of a wide volcano-tectonic and metallogenetic belt that extends from Cabo de Gata to the Sierra de Cartagena (Figure 1). In the study area, the Almanzora river basin (1800km^2) overlies a tectonic basin between two metamorphic ranges, the SA and the Sierra de Almagro, and is filled with Tertiary deposits overlain by the Quaternary alluvial and deltaic deposits of the Almanzora River (Figure 2). The main system of faults occurs in the NE–SW direction parallel to the Palomares fault (Figure 2).

Materials and Methods

Soil and stream sediment samples were collected from standardized methods for sampling and describing contaminated soils (EPA 1991). Detailed metal contamination and composition profiles were determined for the surface soils through local geochemical profiling. This worked from soil core samples taken from areas of high soil contamination near the main tailings disposal area. Tailings samples were obtained by hand-excavation as deep as 0,4 m.
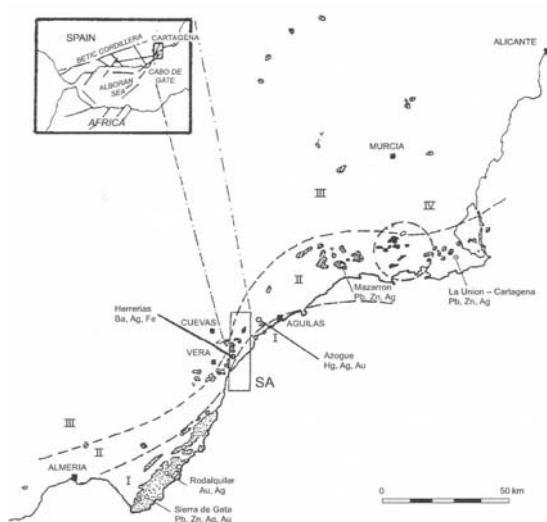
Fig. 1. Location map of the study area and volcanic belt of Cartagena-Gata metallogenic arc. (I) Calc-alkaline lavas Cabo de Gata. (II) K_2O-enriched calc-alcaline volcamic domes. (III) Hyper potassic, aluminous volcanic necks. (IV) Basalts of Cartagena, Modified after López Ruiz & Rodríguez (1980).

Fig.2. Schematic geological map of the SA area. (0) Alluvial Quaternary deposits; (1) Quaternary sedimentary deposits; (2) Upper Miocene volcanic rocks; (3) Miocene sedimentary deposits; (4) Permian-Triassic metamorphic basement; (5) Main faulting system.
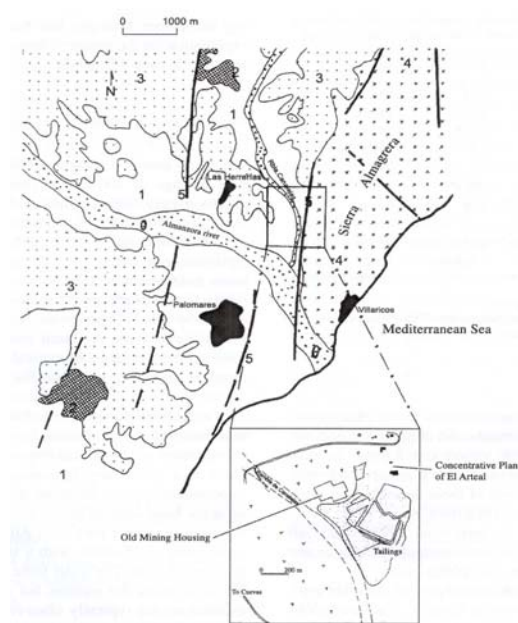
Soil, stream sediment and tailings samples were sealed to minimize exposure to atmospheric gases, and after drying at $30^{\circ}C$ for 48 h, they were prepared in the following ways:

(1)   Homogenization of tailings samples and determination of grain size, porosity, bulk density, pH and electric conductivity.

(2)   Determination of grain size, porosity, bulk density, pH and electric conductivity of soil and stream sediment samples. Chemical analyses were performed on subsamples (<2mm in diameter) from each soil and sediment sample core. The results gave the $CaCO_3$ content, the total N, P, TOC, the gypsum percentage and the cation exchange capacity (CEC). The chemical analyses of tailing samples were done by grinding homogenized samples in a mechanical mortar (Fritsch pulverisette 502).

The total content in metals and trace elements was determined by Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma Emission Spectroscopy (ICP-OES): Au, Ag, As, Ba, and Sb were determined by INAA and Cu, Pb, Zn and Ag by ICP-OES.

Non-sequential extractions were performed on selected tailings, soil and sediment samples to determine the distilled-water soluble fractions (WDE) of each sample. The distilled-water fraction was analyzed by ICP-MS Hewlett Packard 4500 to determine: the Ag, As, Ba, Cu, Pb, Sb and Zn content and the usual methods were utilized to determine the major anions and cations (APHA 1989).

The mineralogy of the tailings and soil samples was examined by X-ray powder diffraction (XRPD).

Results

The results of the mineralogical study (Collado,2002) indicate the most abundant secondary minerals present to be jarosite, natrojarosite, crystalline oxyhydroxide of Fe (goethite), amorphous ferric hydroxide, clay minerals, anglesite, alunite and gypsum, which can occur either as a primary or a secondary phase in the SA. Other secondary phases detected were plumbojarosite, langite and uklonskovite, in minor quantities. The chemical analyses of the samples from the tailings (Table 1) show high concentrations of Ag, As, Ba, Cu, Pb, Sb and Zn. The chemical analyses of the soils and sediments show high amounts of Ag, As, Ba, Pb, Sb, and Zn, though the mean concentrations decrease with respect to the tailings by approximately 50% in the soil (Table 1) and stream sediments of the Rambla de Canalejas, the main tributary of the Almanzora river (Table 1).

Table 1. Summary statistics of tailings, soils and sediments samples of Sierra Almagrera. Values in ppm, except Au (ppb).

Element	Tailings		Soils		Sediments	
	Mean	**S.D.**	**Mean**	**S.D.**	**Mean**	**S.D.**
Au	5,60	3,50	4,40	2,70	6,25	2,60
Ag	29,80	8,80	14,30	11,80	9,75	8,91
As	285,4	82,6	96,9	83,0	91,5	80,4
Ba	54000,0	15798,7	24700,0	27365,7	11750,0	12416,8
Cu	57,7	--	37,5	12,6	--	--
Pb	2687,5	--	1859,1	675,6	--	--
Sb	179,0	65,4	168,5	240,2	65,5	57,8
Zn	2269,0	575,6	815,7	696,9	977,0	709,1

Discussion

The concentrations and mobility of dissolved contaminants within the SA mining area seem to be controlled by a series of precipitation–dissolution reactions, in which the secondary phases are of great importance. Thus, the geochemistry data of distilled water extracts, interpreted using the equilibrium geochemical model PHREEQCI (Parkhurst 1995), suggest that the extractions are saturated to supersaturated with many minerals: calcite, dolomite, celestite, gypsum, jarosite, natrojarosite and iron (oxy)hydroxides (Table 2). In the same way, the leachings from column experiments (Navarro et al, 2004) are saturated to supersaturated with jarosite $KFe_3(SO_4)_2(OH)_6$, amorphous ferric hydroxide and goethite. These phenomena have been detected in other tailings areas, showing the pore water saturation with respect to jarosite, natrojarosite and gypsum (1998; Al *et al.* 2000). Most of these secondary phases were detected by X-ray powder diffraction (Table 2) suggesting the remobilization in the soil of Ba, Cu, Pb and Zn from secondary phases that had precipitated when the soil and pore water conditions favored their precipitation. Along these lines, Bigham and Nordstrom (2000) indicate that 'the rapid dissolution' of accumulated soluble salts during subsequent rainfall events may release acidity and produce 'pulses' of contaminants into the environment. The column experiments (Navarro et al, 2004) correspond to the geochemical and X-ray data, which show a 'kinetic' dissolution of most secondary phases and the mobilization of Cu, Pb and Zn, while the low/negligible mobility of Ag, As and Sb can be associated with secondary phases of low solubility or sulfides of a lowoxidation rate. The low mobilization of Ag, As and Sb in the column experiments is consistent with those phase minerals that were detected by X-ray, since we have not detected soluble secondary

phases like Fesulfoarsenates, or valentinite, whose dissolution can produce the mobilization of these elements. These results suggest that the mobilization of Pb can be caused by the dissolution of secondary anglesite and plumbojarosite, which was also detected as a secondary phase and/or desorbed from reactive surfaces (Al *et al.* 2000), or by the dissolution of jarosite, in which the Pb content may reach high amounts (Gieré *et al.* 2003).

Table 2. Saturated phases of water extraction from soils, calculated bu PHREEQCI (1) and phase minerals detected by X-ray powder difraction (2).

Mineral	Component Formula	1	2
Alunite	$K[Al_3(OH)_6(SO_4)_2]$		X
Anglesita	$PbSO_4$		X
Anhydrite	$CaSO_4$	X	X
Calcite	$CaCO_3$	X	X
Celestite	$SrSO_4$	X	X
Ferrihydrite	$5Fe_2^{3+}O_3 \cdot 9\ H_2O$	X	X
Gibbsite	$Al(OH)_3$	X	X
Goethite	$\alpha-Fe^{3+}OOH$	X	X
Gypsum	$CaSO4 \cdot 2H_2O$	X	X
Hausmannite	$Mn^{2+}Mn_2^{3+}O_4$	X	X
Hematite	Fe_2O_3	X	
Hydronium jarosite	$(H_3O^+)_2Fe^{3+}{}_6(SO_4)_4(OH)_{12}$	X	X
Jarosite	$K_2Fe_6^{3+}(SO_4)_4(OH)_{12}$	X	X
Langite	$[Cu_4(OH)_6(H_2O)(SO_4)]H_2O$		X
Lepidocrocite	$\gamma-Fe^{3+}OOH$	X	X
Melanterite	$(Fe, Zn, Cu)SO_4 \cdot 7\ H_2O$		X
Natrojarosite	$Na_2Fe^{3+}{}_6(SO_4)_4(OH)_{12}$	X	X
Plumbojarosite	$Pb[Fe_3(OH)_6(SO_4)_2]_2$		X
Siderite	$Fe^{2+}CO_3$	X	X
Uklonskovite	$Na[MgF(H_2O)_2(SO_4)]$		X

The mobilization of Cu can be caused by langite, melanterite or brochantite / calcantite (also detected in minor quantities) dissolution and desorption from iron oxyhydroxides and organic matter. Whether mobilization of Ba occurs is still unclear. The mobilization of Zn can be originated by the dissolution of melanterite and goslarite and/or desorption processes.

Conclusions

The geochemical data of contaminated soils and stream sediments, indicate elevated levels of Ag, As, Ba, Cu, Pb, Sb and Zn. The concentrations of As, Pb and Zn exceed the intervention values established in the Andalusian Regulations for Contaminated Soil. The oxidation of sulfides and sulfosalts causes the precipitation of secondary phases like 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 ($KAl_3(SO_4)_2(OH)_6$), gypsum ($CaSO_4 \cdot 2H_2O$), and other less abundant mineral phases. The geochemistry data of distilled water extracts from soils and column experiments indicate that the extractions and leachings are saturated to supersaturated with many minerals, namely calcite, dolomite, gypsum, jarosite, and iron (oxy)hydroxides. These results suggest that the secondary phases have the potential to serve as a sink for dissolved contaminants in dry periods and also to serve as a stock of mobilizable elements when, in humid periods, rainwater dissolves the secondary minerals.

Literature cited

Al TA, Martin CJ, Blowes DW. 2000. Carbonate-mineral/water interactions in sulphide-rich mine tailings. Geochimica et Cosmochimica Acta 23, 3933–3948.

APHA. 1989. Standard Methods for the Examination of Water and Wastewater, 17th edn. Washington: APHA.

Appelo CAJ, Postma D. 1996. Geochemistry Groundwater and Pollution. Rotterdam: Balkema, 536pp.

Collado D. 2002. Movilización de contaminantes en el terreno a partir de Suelos Contaminados, MSc Thesis, Universidad de Granada.

EPA. 1991. Description and Sampling of Contaminated Soils. A Field Pocket Guide. EPA/625/12-91/002.

EPA. 1996. Managing Environmental Problems at Inactive and Abandoned Metal Mine Sites, E.P.A./625/R-95/007, Washington.

Gieré R, Sidenko NV, Lazareva EV. 2003. The role of secondary minerals in controlling the migration of arsenic and metals from high-sulfide wastes (Berikul gold mine, Siberia). Applied Geochemistry 18, 1347–1359.

López Ruiz J, Rodríguez E. 1980. La región volcánica neógena del sureste de España. Estudios Geológicos 36, 5–63.

Navarro A, Collado D, Carbonell M, Sánchez, J.A. 2004. Impact of minig on soils in a semi-arid environment: Sierra Almagrera district, SE Spain. Environmental Geochemistry and Health. 26, 383-394.

Parkhurst D L. 1995. Users Guide to PHREEQC–a Computer Program for Speciation, Reaction-Path, Advective-Transport, and Inverse Geochemical Calculations, U.S. Geological Survey, Water – Resources Investigations Report 95 –4227.