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Geochemistry of Metals from Mine Tailings in Taxco, Mexico

M. A. Armienta,[1] O. Talavera,[2] O. Morton,[1] M. Barrera[3]

[1] Geophysics Institute, National Autonomous University of Mexico, Circuito Exterior, C.U., México 04510 D.F., Mexico
[2] Regional Center of Earth Sciences, Autonomous University of Guerrero, Taxco, Guerrero, Mexico
[3] Graduate Program, Geophysics Institute, National Autonomous University of Mexico, Circuito Exterior, C.U., México 04510 D.F., Mexico

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Mining is one of the most important economic activities of Mexico since the 15th Century. In contrast to its economic benefit, different kinds of residues associated with the extraction and processing of metals accumulated along centuries, constitute potential environmental pollution sources. In central-southern Mexico, Taxco has been one of the main silver producing locations since prehispanic times. Mineralogy reported in Taxco includes lead, silver, copper, iron and zinc ores like pyrite (FeS_2), esphalerite (ZnS), galena (PbS), chalcopyrite ($CuFeS_2$), argentite (Ag_2S), native silver, polibasite ($(AgCu)_{16}Sb_2S_{11}$), proustite (Ag_3AsS_3) and pyrargirite (Ag_3SbS_3). The gangue is formed by a variety of minerals including quartz (SiO_2), calcite ($CaCO_3$), magnetite (Fe_3O_4), barite ($BaSO_4$), hematite (Fe_3O_4), and rodhocrosite ($MnCO_3$) (Talavera et al., 2001). Over 20 million Tons of tailings generated from the processing of Ag, Au, Pb, Cu and Zn, were deposited in several impoundments inside and near the city (Fig. 1).

It is widely known that oxidation of sulfide minerals from mine waste material can generate acid mine drainage (AMD), that produces high concentrations of dissolved sulfate and metals (Ritcey, 1989; Salomons, 1995). When the acid solution comes in contact with other minerals in the tailings, a serial of chemical reactions occurs. If carbonate is present in the system, an alkaline carbonate solution may neutralize the acid generated by the oxidation of sulfide minerals (Lin, 1997; Al et al, 2000). Secondary and tertiary minerals may also be produced within the tailings (Jambor, 1994). The mobility of metals released from sulfide oxidation is thus affected by the formation of these minerals. Metal content, mineralogy and physico-chemical conditions determine the potential of environmental pollution by metals and metaloids from tailing impoundments (Blowes and Jambor, 1990; Johnson et al., 2000). Furthermore, the geochemical and mineralogical study of the mining wastes can help to understand the problem of acid mine drainage and to develop an efficient remediation program.

Mining is currently active in many parts of México. Nevertheless, few environmental studies have been carried out on new or old mining wastes (Castro et al., 1997; Manz and Castro, 1997; Carrillo and Drever, 1998). In the Taxco mining district there are tailing impoundments of various ages and sizes (La Concha, Sta. Rosa, Taxco and El Fraile). The present study focuses on the El

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Correspondence to: M. A. Armienta

Fraile tailing area near the El Fraile town. Its location on the Cacalotenango river shore, and at a distance of about 10m from the nearest house, makes its characterization and risk evaluation specially relevant (Fig. 1).

MATERIALS AND METHODS

To evaluate their potential to affect the environment, samples were collected for chemical and mineralogical analyses. The samples were taken from different areas on the tailing's walls showing different visible characteristics, digging with a shovel until the appearance of less altered material. Samples were air-dried, quartered and sieved through a 1.70 mm mesh. The mineralogical and physico-chemical determinations were performed on the sieved sample.

X-ray diffraction determinations were performed with a JEOL DX-GERP12 powder diffractometer with CuK_{α} radiation to identify the major minerals present in the tailings. Metal contents (Zn, Pb, As, Fe) were analyzed by ICP-MS. Tailing samples were leached with water to determine pH, and the soluble fraction of metals and sulfate.

Total metals were determined digesting 0.2 g of sample with a mixture of concentrated acids (5 ml HNO_3 and 10 ml $HClO_4$). The solution was evaporated to dryness and the residue was subsequently dissolved and diluted to 100 ml with HNO_3 2 %. The analyses were carried out by ICP-MS at the Instituto de Geofísica, Universidad Nacional Autónoma de México. The ICP mass spectrometer used was a VGElemental model PQ3. Detection limits are calculated as the concentration equivalent to three times the standard deviation of five replicates of the blank solution. For all elements it was better than 50 ppt. Calibration was performed with a 1, 10, 100 and 200 ppb multi-elemental standard solution (SPEX- High Purity) and a blank solution of de-ionized water, all containing HNO_3 at 2%. Matrix effects and instrumental drift were eliminated by using ^{115}In (10 ppb) as internal standard. The validity of the analytical procedure was assessed on accuracy and precision tests. These were calculated by comparing a measured and a Standard Reference Material (SRM-2586) obtained from the National Institute of Standards & Technology. All elements have a precision better than 10 % RSD (relative standard deviation).

Twenty grams of the sample were added with 100 ml of deionized water, agitated for one hour and filtered through 0.45 µm. The filtrate was used for conductivity and sulfate determinations. One gram was added with 10 ml of deionized water for the pH measurement by potentiometry. Conductivity and pH were determined with a Conductronic PC18. The equipment was calibrated with pH=4 , pH=7 and pH=10 buffers and with a solution of 1000 mg/L of NaCl corresponding to a conductivity value of 1990 µS/cm. Sulfate was analyzed by turbidimetry (Armienta et al., 1994) with a uv-visible diode array spectrophotometer Hewlett Packard 8452a.

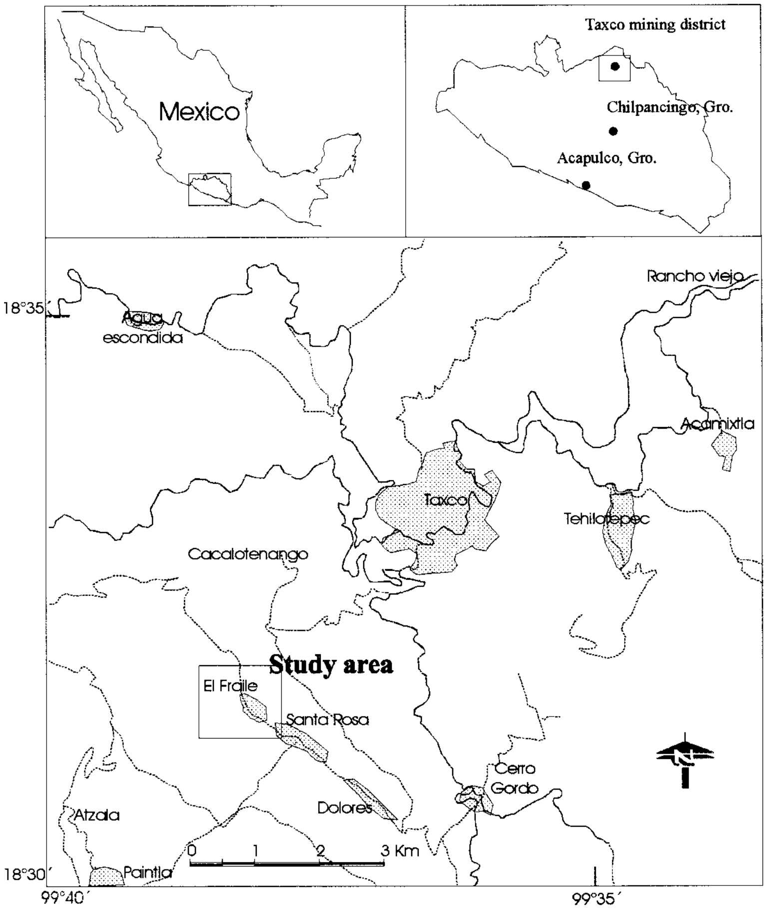

Figure 1. Study area.

RESULTS AND DISCUSSION

The main minerals identified by XRD are presented in Table 1. Samples JF2 and JF3 (Group I) showed the same mineralogical assemblage, with calcite as the predominant phase and pyrite in a low content. The other samples did not contain these minerals (Group II). Quartz was the predominant phase in the rest of the samples. Gypsum was present in different proportions in all the samples. On the other hand, samples without pyrite contained jarosite or argentojarosite. Illite was identified in only one of the samples.

Total metal concentrations are shown in Table 2. High concentrations of all the analyzed metals were measured in the samples. The highest contents of Zn (20,200 ppm), As (2053 ppm), Fe (13670 ppm) and Pb (22900 ppm) were found in Group I samples. This group had also near neutral pH values and lowest conductivity; in contrast, acid values were found in the rest of the samples (Group II).

The two tailing groups can also be distinguished according to their visible characteristics. White color predominated in the tailings of Group I, compared to the brownish to red color of the tailings from Group II. The pH, chemical and mineralogical composition of the analyzed samples were also different between the two groups.

Table 1. Mineralogy of the analyzed samples .

Sample	Calcite	Quartz	Pyrite	Gypsum	Jarosite	Argento-Jarosite	Illite
JF1		XXXX		XXX		X	X
JF2	XXXX	XXX	XX	X			
JF3	XXXX	XXX	XX	X			
JF4		XXXX		X	XXX		
JF5		XXXX		XXX	XXX		
JF6		XXXX		X	XXX		
JF7		XXXX		XXX	X		
JF8		XXXX	X	XXX	X		
JF9		XXXX		XXX	X		
JF10		XXXX		X	XXX		

(XXXX= Predominant, XXX= Abundant, XX= Low, X= Very low)

Table 2. Metal concentration of the analyzed samples (mg/kg), pH, Λ (μS/cm), and SO_4^{2-} (mg/l).

Sample	pH	Λ	$SO4^{2-}$	Zn	Pb	As	Fe
JF1	2.5	3890	2518	1422	455	201	12550
JF2	6.7	2215	1377	20200	22900	1875	13220
JF3	7.0	2225	1322	5924	4086	2052	13670
JF4	2.4	5510	7809	1730	5093	469	9960
JF5	2.3	4960	4707	1067	6033	991	9100
JF6	2.4	4965	4674	864	6351	412	8000
JF7	2.6	3385	1750	427	4361	586	7100
JF8	2.9	2615	1450	501	3229	731	9443
JF9	2.7	3205	1802	591	4772	461	8570
JF10	2.4	6660	9129	1762	2421	711	9458

Table 3. Average heavy metals total and soluble concentrations (mg/kg) in the analyzed tailings.

	Group I		Group II	
	Total	Soluble	Total	Soluble
Zn	13062	37 (0.3%)	1045	457 (43.7%)
Pb	13493	0.5 (0.004%)	4089	2.4 (0.06%)
As	1964	0.4 (0.02%)	571	13.4 (2.4%)
Fe	13445	nd	9275	1843 (20%)

(nd=non detectable)

The average total metal contents of Group I was higher than those of Group II and the soluble contents were lower (Tables 2 and 3). The highest total concentrations of all the metals in Group II corresponded to Fe (9275 mg/kg) whereas Pb was the metal present in highest concentration in Group I (13493 mg/kg). Arsenic had the lowest concentration in both groups. Highest soluble percentage corresponded to Zn in both groups. Low soluble Pb percentages were present in both groups (0.06% in Group II and 0.003% in Group I). Higher soluble proportion in Group II was determined for As (2.4%) regarding Group I (0.02%). Soluble Fe had contrasting values, 1843 mg/kg (20 %) in Group II, whereas in Group I it could not be detected.

The tailings normally contain a variety of residual sulfides like pyrite (FeS_2), galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$) and arsenopyrite (AsFeS). The oxidation of sulfide minerals is inferred from the low-pH Group II samples, which in turn have the highest concentrations of dissolved metals and SO_4^{2-}.

Metal release as a result of sulfide oxidation was also evident from the correlation between soluble metals (Zn, As, Fe) and sulfate concentrations of some samples of group II (Figure 2). Lack of correlation for some samples may result from the hetereogeinity of the tailings. The results show that the increase of carbonate contents (observed in Group I) in the tailings favors a major removal of heavy metals in the extractable fraction and neutralizes the acid mine drainage.

Precipitation-solubilization and sorption reactions may explain the different soluble ratios observed in both Groups. Zn and Pb may be forming sulfate compounds at acid pHs' and carbonates at near neutral pH's. The higher solubility of sulfates regarding carbonates may explain the greater soluble fractions found in Group II for both metals. The low solubility of hydroxide and carbonate iron compounds may explain the non detectable concentration found in the soluble fraction in Group I. On the other hand, the higher solubility of sulfate iron compounds like jarosite in acid medium could explain the high soluble Fe ratio found in Group II. The arsenic percentage in the soluble fraction may be influenced mainly by co-precipitation and sorption reactions on iron oxyhydroxides. These processes may control the As release from the tailings.

The highest soluble metal contents found in Group II were above the international drinking water guidelines (As = 0.01 mg/L, Pb = 0.01 mg/L , Zn = 3 mg/L) (WHO, 1993). Soluble content of Zn, As and Pb although lower in Group I than in Group II, was also above the international water guidelines.

This geochemical and mineralogical study suggests that the El Fraile tailings have high metal-rich acid drainage formation potential. Those tailings constitute a potential risk to the environment and the community of El Fraile.

The ability of the carbonate to control the retention of metal and neutralize the acid generated by sulfide oxidation, can be used in developing a remedial action plan for the El Fraile area.

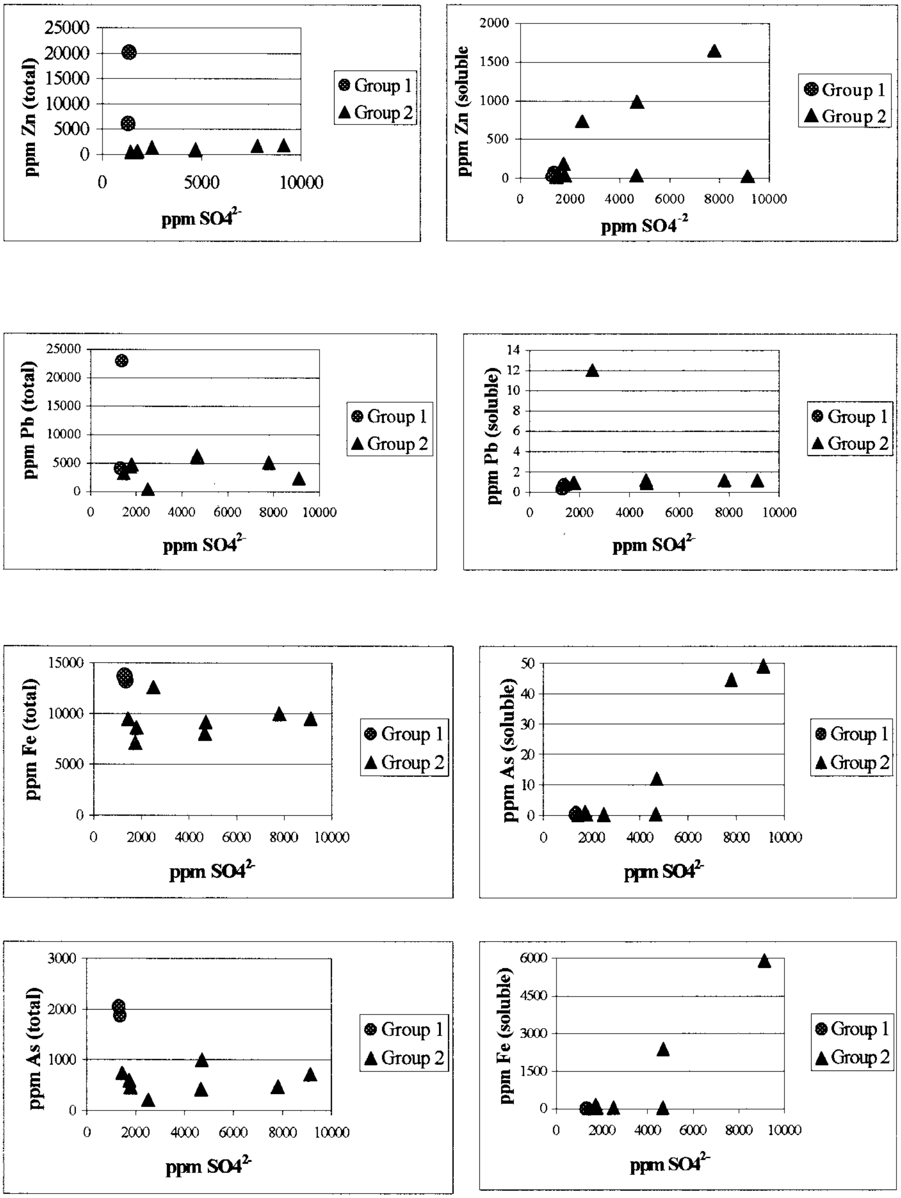

Figure 2. Total and soluble metals versus sulfate concentrations.

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REFERENCES

Al TA, Martin JC, Blowes DW (2000) Carbonate-mineral/water interactions in sulfide-rich mine tailings, Geochim Cosmochim Acta 64: 3933-3948.

Armienta MA, Zamora V and Juárez F (1994) Manual para el Análisis Químico de Aguas Naturales en el Campo y en el Laboratorio, Comunicaciones Técnicas IGF, Serie Docencia y Divulgación No.4, 86pp.

Blowes DW, Jambor JL (1990) The pore-water geochemistry and the mineralogy of the vadose zone of sulfide tailings, Waite Amulet, Quebec, Canada. Appl Geochem 5: 327-346.

Carrillo A, Drever JI (1998) Environmental Assessment of the potential for arsenic leaching into groundwater from mine wastes in Baja California Sur, Mexico. Geofisica Internacional 37:35-39.

Castro J, Kramer U, Puchelt H (1997) 200-year mining activities at La Paz, San Luis Potosí/Mexico -consequences to environment and geochemical exploration. J Geochem Explor 58: 81-91.

Jambor JL (1994) Mineralogy of sulfide-rich tailings and their oxidation products. In: Blowes DW, Jambor JL (eds.) The environmental geochemistry of sulfide mine-wastes. Mineralogical Association of Canada, Waterloo, pp 59-102.

Johnson RH, Blowes DW, Robertson WD, Jambor JL (2000) The hydrogeochemistry of the Nickel Rim mine tailings impoundment, Sudbury, Ontario. J Cont Hydrol 41: 49-80.

Lin Z (1997) Mobilization and retention of heavy metals in mill-tailings from Garpenberg sulfide mines, Sweden. Sci Tot Environ 198: 13-31.

Manz M, Castro J (1997) The environmental hazard caused by smelter slags from the Sta. Maria de la Paz mining district in Mexico. Environ Pollut 98: 7-13.

Ritcey G.M. (1989) Tailings Management. Problems and solutions in the mining. Elsevier.

Salomons W (1995) Environmental impact of metals derived from mining activities: Processes, predictions, prevention. J Geochem Explor 52:5-23.

Talavera MO, Armienta MA, Moreno TR, Yta M (2001) Impacto ambiental de los metales pesados en la región minera de Taxco Guerrero, México, XI Congreso Latinoamericano de Geología, Uruguay, Uruguay.

World Health Organization (1993) Guidelines for drinking-water quality, 2nd ed., Geneva.