

## Geochemistry of leachates from the El Fraile sulfide tailings piles in Taxco, Guerrero, southern Mexico

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### Abstract

Leachates from the El Fraile tailings impoundment (Taxco, Mexico) were monitored every 2 months from October 2001 to August 2002 to assess the geochemical characteristics. These leachates are of interest because they are sometimes used as alternative sources of domestic water. Alternatively, they drain into the Cacalotenango creek and may represent a major source of metal contamination of surface water and sediments. Most El Fraile leachates show characteristics of Ca–SO<sub>4</sub>, (Ca + Mg)–SO<sub>4</sub>, Mg–SO<sub>4</sub> and Ca–(SO<sub>4</sub> + HCO<sub>3</sub>) water types and are near-neutral (pH = 6.3–7.7). Some acid leachates are generated by the interaction of meteoric water with tailings during rainfall events (pH = 2.4–2.5). These contain variable levels of SO<sub>4</sub><sup>2-</sup> (280–29,500 mg l<sup>-1</sup>) and As (<0.01–12.0 mg l<sup>-1</sup>) as well as Fe (0.025–2352 mg l<sup>-1</sup>), Mn (0.1–732 mg l<sup>-1</sup>), Zn (<0.025–1465 mg l<sup>-1</sup>) and Pb (<0.01–0.351 mg l<sup>-1</sup>). Most samples show the highest metal enrichment during the dry seasons. Leachates used as domestic water typically exceed the Mexican Drinking Water Guidelines for sulfate, hardness, Fe, Mn, Pb and As, while acidic leachates exceed the Mexican Guidelines for Industrial Discharge Waters for pH, Cu, Cd and As. Speciation shows that in near-neutral solutions, metals exist mainly as free ions, sulfates and bicarbonates, while in acidic leachates they are present as sulfates and free ions. Arsenic appears as As<sup>(V)</sup> in all samples. Thermodynamic and mineralogical evidence indicates that precipitation of Fe oxides and oxyhydroxides, clay minerals and jarosite as well as sorption by these minerals are the main processes controlling leachate chemistry. These processes occur mainly after neutralization by interaction with bedrock and equilibration with atmospheric oxygen.

### Introduction

The Taxco mining district in southern Mexico was one of the richest producers of precious metals (Ag and Au) in the Americas during colonial (1523–1810) times. Throughout much of the 20th century, Taxco mines were renowned for their production of base metals (Cu, Pb and Zn) and Ag. More than 450 years of intensive mining activity has resulted in the discharge of large quantities of tailings and mining wastes into

surrounding areas. Most of the colonial waste was re-extracted or buried during the 20th century and, consequently, there is little evidence left of the earliest mining activities. In contrast, rock wastes and mill tailings generated during modern (1920 to present) times are easily recognizable through the Taxco district, and because some of these tailings are located within communities, they have become a matter of both environmental and health concern. In some communities, people occasionally use leachates as an alternative source of domestic

water during the dry (winter/spring) seasons. As a result of this activity, knowledge of the geochemistry and quality of these leachates has become an important issue in the area. There are as yet no reported studies on the leachates in Taxco, although a limited number of recent studies on the environmental impact of mine wastes in nearby areas have been carried out (Flores-Mundo 2002; Armienta *et al.*, 2003, 2004; Talavera Mendoza *et al.*, 2005).

In this paper, we report the geochemical characteristics and seasonal variations for leachates from the El Fraile tailings deposit located in Taxco, Guerrero, southern Mexico. The El Fraile tailings impoundment is located approximately 12 km SW of Taxco City and contains tailings produced between 1940 and 1970 (Figure 1). The tailings are in two accumulations that are settled on the shores of adjacent tributaries of the Cacalotenango Creek. They lie directly on low-permeability calcareous sandstones and shales that facilitate drainage of tailings leachates into the creek. Conservative calculations indicate that these two deposits contain around 5 million tons

of tailings. The objective of this study was to compare characteristics of leachate samples occasionally used as domestic water with the Mexican Drinking Water Guidelines (MDWG; NOM-127-SSA1-1997) in order to evaluate the risk of the leachates to public health and to compare the remaining leachate samples with the Mexican Guidelines for Industrial Discharge Waters (MGIDW; NOM-002-ECOL-1996) to assess the environmental impact of the leachates to surface water and sediments. Speciation and saturation indices (SI) are calculated and discussed together with previously published mineralogical data in order to elucidate the main processes controlling water chemistry and quality.

### Sampling and analytical methods

Fifteen sites of major leachate discharge were identified in the El Fraile tailings. Eight representative sites, JF-01 to JF-08, were selected and sampled every 2 months from October 2001 to August 2002. Sampling sites were chosen based on

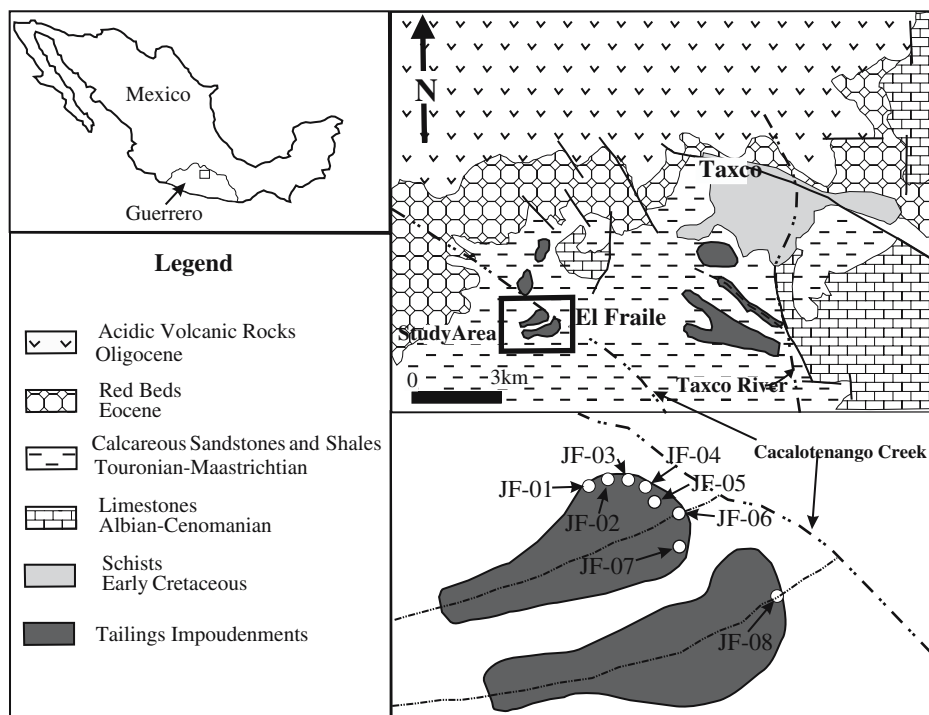


Fig. 1. Geologic map of the Taxco, Guerrero region after Campa and Ramírez (1979) showing the localization of El Fraile tailings deposits and the location of sampling points JF-01 to JF-08.

their discharge volume and usage. The location of the sampling points is shown in Figure 1. In the El Fraile region the main rainy season occurs in the summer (June–September) with sporadic rains in the fall (October–December). Thus, the main dry season occurs during the winter and spring (January–May). Sample JF-01 comes from a faucet sporadically used as a domestic water supply source. Samples from sites JF-02, JF-06 and JF-08 are waters from discharge tunnels, two of which (JF-02 and JF-08) constitute an alternative source of domestic water for many homes. Samples JF-03 and JF-04 come directly from hoses conducting leachates to these homes. Sample JF-05 is a surface accumulation formed by the interaction of meteoric water with tailings during rainfalls. Finally, sample JF-07 comes from a discharge tube surrounded by a great accumulation of secondary Fe-oxyhydroxides and efflorescent minerals.

Samples were taken in duplicate in the form of a 1-l aliquot for anion analyses and a 500-ml aliquot acidified with 2.5 ml of concentrated ultra pure Ultrex II nitric acid for cation analyses. In the field, pH, temperature, electrical conductivity and redox potential were measured with portable electrodes. Samples were analyzed in the Geochemistry Laboratory, Universidad Autónoma de Guerrero. Alkalinity and chlorides were determined by titration with 0.02 M HCl and 0.01 M AgNO<sub>3</sub>, respectively. Sulfates were measured with a Hach DR890 Colorimeter using the BaCl<sub>2</sub>-acetic acid procedure. Total dissolved solids (TDS) were determined gravimetrically. Metals and metalloids, with the exception of sodium, were determined by inductively coupled plasma-atomic emission spectra (ICP-AES) using a Perkin Elmer Optima 3200 DV (Perkin Elmer, Foster City, Calif.) following the filtration of acidified samples through 0.45- $\mu$ m cellulose nitrate membrane filters. Sodium was measured by a flame atomic absorption spectrophotometer (FAAS) in acidified and filtered samples using a Perkin Elmer Analyst 100 instrument. Four High-Purity Certified Standards of Wastewater (CWW-TM-D; CWW-TM-H; CWW-TM-A and CWW-TM-E) were run with the samples to check accuracy and precision. The lowest concentration for each metal was (in milligrams per liter): Ag and Cd, 0.005; Ba, As, Pb, Se, Mo and Sb, 0.010; Fe, Mn, Co and Cu, 0.025. These values are considered the detection limit. Geochemical speciation and the SI of the dissolved

elements were determined using the PHREEQC (Pankhurst 1995) equilibrium models with the WATEQ4F database (Ball & Nordstrom 1991).

### Economic geology and description of the El Fraile tailings

Bedrock in the Taxco area is comprised of schists, limestones, sandstones, shales, red beds and acidic volcanic rocks whose ages range from the Cretaceous to the Oligocene (Figure 1). Mineralization has occurred in hydrothermal veins, replacing structures and stockworks hosted in limestone, and more rarely in schist and red beds. Vein trends range from north to south to N60°W and coincide with major regional structures (Campa & Ramírez 1979). Mineralized structures are 1–3 m in width (although a few reach 10 m) and 700–2000 m long. Main ores include galena, chalcopyrite, sphalerite, native silver, argentite and Ag-bearing (polybasite, proustite, pyrargirite) sulfosalts, whereas gangue phases include pyrite, pyrrhothite, quartz, barite, calcite, rhodochrosite, hematite, tremolite, epidote and ilvaite (Consejo de Recursos Minerales 1999).

The El Fraile tailings deposit is characterized by flat dams that are typical of sites constructed with oversaturated mud. Very fine- and fine-sand grain sizes predominate in the tailings, and the organic matter content is low (Flores-Mundo 2002). In both deposits, the dams were covered with a thick bed of sterile material to stabilize the tailings and to minimize aerial dispersion. In general, tailings are oxidized and have developed a widespread 3- to 5-cm-thick ochreous crust. Non-oxidized tailings can still be found as small, isolated, grey-colored patches.

Studies by Flores-Mundo (2002), Armienta *et al.*, (2003) and Talavera Mendoza *et al.*, (2005) indicate that the oxidation of tailings and subsequent neutralization via calcite and Fe-oxyhydroxides produce near-neutral leachates with appreciable amounts of As as well as Fe, Zn, Cd and Mn. Mineralogical characterization shows that the major primary phases are dominated by quartz with minor amounts of feldspars and ferromagnesian minerals. Calcite is present in the non-oxidized tailings. Sulfides include pyrite, sphalerite, galena, chalcopyrite, bornite and minor Ag-sulfosalts and appear preferentially in non-oxidized tailings. The secondary phases include

gypsum, jarosite, bernalite, hematite, magnetite, epsomite, basanite, smithsonite and clay minerals.

## Results

### *Physico-chemical parameters and major ions of leachates*

The chemical parameters and major ions in leachates from the eight sampling sites are reported in Table 1. Seasonal variations of selected physico-chemical parameters and major ions are shown in Figure 2. The temperature of the leachate samples ranged from 16.1 to 26.5°C, which is very close to seasonal temperatures. Only site JF-05 showed significant temperature variations. Seven of the eight sample sites had near-neutral leachates with pH values ranging between 6.3 and 7.7. Seasonal variation within each near-neutral sample was less than 0.5 pH units, which is not significant (Figure 2a). Site JF-05 was acidic in nature with pH values ranging from 2.4 to 2.5, which is below the lower limit of the MGIDW (5.5–10.0).

Sample site redox potential (Eh) values varied from +76 to +740 mV, with most falling in the range reported for surface waters (Table 1) (Drever 1997). Five of the sample sites showed little seasonal variation in Eh (Figure 2b). For the remaining three sample sites, JF-05 was the most oxidized, with Eh values ranging from +655 to +740 mV, JF-03 showed seasonal variations without a trend and JF-02 samples exhibited a lower Eh at the beginning of the rainy season.

The conductivity of leachates was variable but consistently high, ranging from 1.0 to 4.9 mS cm<sup>-1</sup> for all samples except JF-05. Sample JF-05 exhibited even greater conductivity, ranging from 6.5 mS cm<sup>-1</sup> (June, 2002) to as high as 21.0 mS cm<sup>-1</sup> (December, 2001) (Table 1). In contrast with the other parameters discussed so far, conductivity showed significant seasonal variations. Three patterns of seasonal behavior were observed: (1) site JF-01 showed a slight increase in conductivity from the first to the second sampling period and then a systematic decrease; (2) sites JF-06 and JF-08 had the highest values during dry sampling times; (3) sites JF-02, JF-03, JF-04 and JF-07 had flat patterns with no major seasonal variations. The TDS values were also

variable and correlated well with conductivity, ranging from 537 to 59,185 mg l<sup>-1</sup> with the acidic JF-05 site samples having the highest values (Table 1).

The HCO<sub>3</sub><sup>-</sup> content of the site samples was variable, ranging from zero in the acidic JF-05 site to 598 mg l<sup>-1</sup> in the JF-07 site. All samples showed a rather homogeneous seasonal behavior with the highest concentrations recorded during the dry seasons (Figure 2d). Sulfate concentrations were generally high, ranging from 280 to 29,500 mg l<sup>-1</sup>, with the highest concentration associated with the acidic site (from 8,411 up to 29,500 mg l<sup>-1</sup>). Sites JF-06, JF-07, and JF-08 showed seasonal variation, recording the highest SO<sub>4</sub><sup>2-</sup> concentrations during the fourth (spring) sampling period (Figure 2e). Other sites did not show significant seasonal variations. Sites JF-01, JF-03, JF-04 and JF-08, which are occasionally used as domestic water sources, all exceeded the MDWG (400 mg l<sup>-1</sup>) guidelines with respect to SO<sub>4</sub><sup>2-</sup> content for all sampling periods (except sample JF-08 during the first sampling period). Chloride content was low to moderate and fell in the range of 6.7 to 23.0 mg l<sup>-1</sup> in all of the samples tested (Table 1).

Calcium and magnesium content was variable, ranging from 152 mg l<sup>-1</sup> to 562 mg l<sup>-1</sup> and from 36 mg l<sup>-1</sup> to 2,733 mg l<sup>-1</sup>, respectively. Total hardness (as CaCO<sub>3</sub>) varied from 552 mg l<sup>-1</sup> to 12,175 mg l<sup>-1</sup>. The acidic site recorded the highest magnesium concentration during the second (winter) sampling period (Table 1). Seasonal variations of calcium were different in all sites, although some of them (JF-02, JF-06, JF-08) recorded the highest enrichments in dry seasons (Figure 2f). Magnesium only showed important seasonal differences in sites JF-06, JF-07 and JF-08, whereas other sites did not have significant seasonal variations (Figure 2g). Calcium and magnesium are not considered in the MDWG, but hardness is. All sites used as domestic water sources exceeded the MDWG for hardness (500 mg l<sup>-1</sup> as CaCO<sub>3</sub>) for all sampling times. Finally, sodium and potassium concentrations were relatively low, ranging from 9.18 to 36.10 mg l<sup>-1</sup> and 3.0 to 40.5 mg l<sup>-1</sup>, respectively. Sodium did not show any seasonal pattern at any of the sites, whereas potassium showed major temporal variations at some sites (JF-06, JF-07 and JF-08), with the highest concentrations occurring during the dry seasons (Figure 2h). At



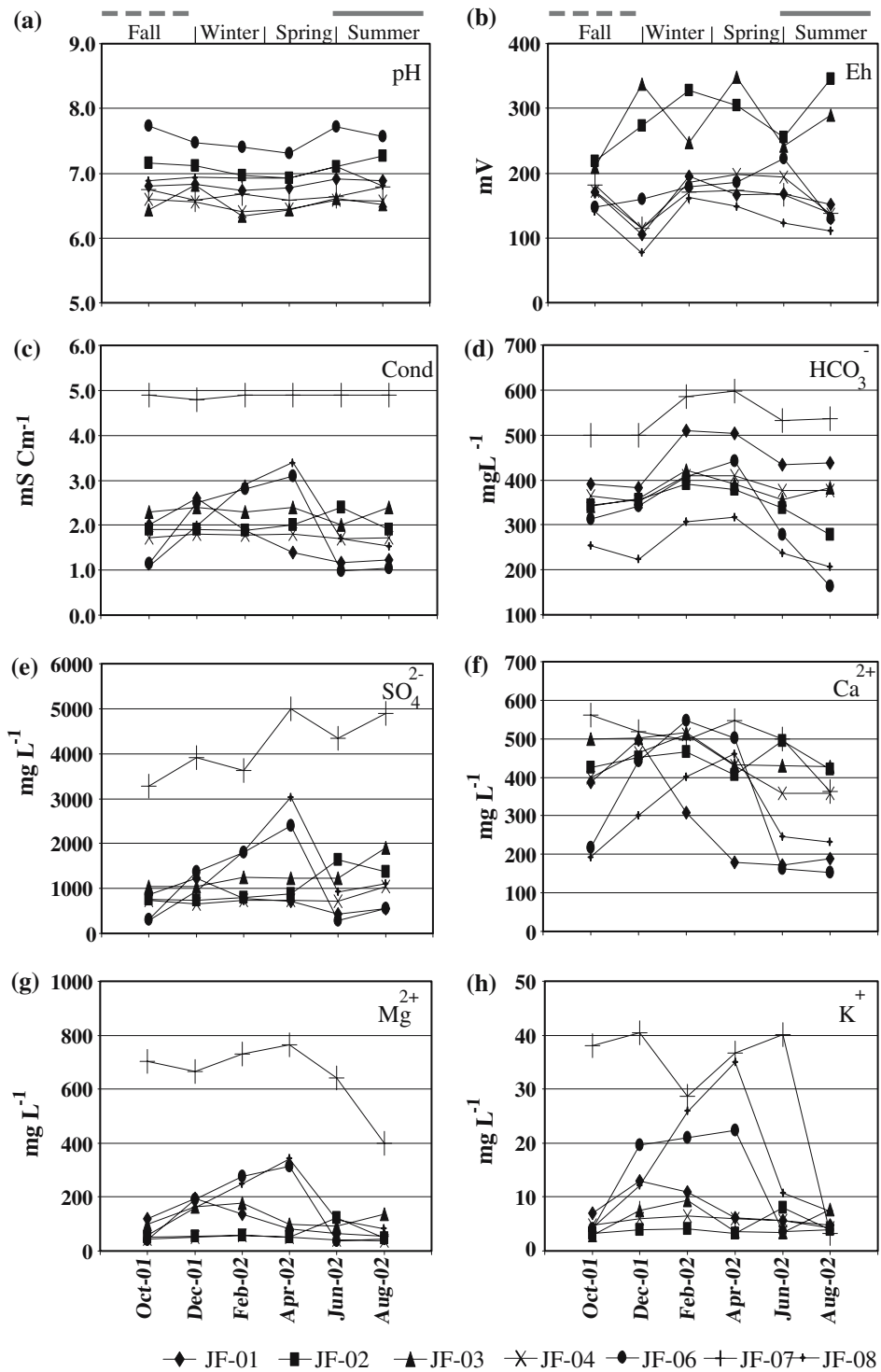


Fig. 2. Seasonal variations of selected physical parameters and major ions in leachates from El Fraile tailings, Taxco, Mexico.

some sites, the potassium content drastically decreased during the rainy season. No site exceeded the MDWG ( $200 \text{ mg l}^{-1}$ ) for sodium.

A Piper diagram of the second and fifth sampling period from each site is shown in Figure 3. Only the data from these two sampling periods are shown due to the similarity of the data across all sampling periods. The shadowed areas in the diagram represent all of the samples studied. This diagram shows that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  appear to be the dominant cations, whereas  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  represent the dominant anions. On this basis, studied leachates can be categorized as waters of the  $\text{Ca-SO}_4$ ,  $(\text{Ca} + \text{Mg})\text{-SO}_4$ ,  $\text{Mg-SO}_4$  or the  $\text{Ca-(SO}_4 + \text{HCO}_3)$  types. These water types are commonly reported from mining environments (see Ritcey 1989; Lee & Lee 2001; Lee 2003).

#### Trace elements

The following metals were below the detection limit for all samples taken: Ag, Co, V, Sb, Mo and

Se. Copper and Cd were below the detection limit in near-neutral samples, but in acidic samples they ranged from  $9.0$  to  $26 \text{ mg l}^{-1}$  and from  $3.6$  to  $11 \text{ mg l}^{-1}$ , respectively. The acidic site, JF-05, exceeded the MGIDW for Cu during the second sampling period, whereas for Cd the guideline was exceeded in both the second and fifth sampling periods. Barium concentrations were generally low, including site JF-05, ranging between  $<0.01$  and  $0.1 \text{ mg l}^{-1}$ . No samples exceeded the MDWG ( $0.7 \text{ mg l}^{-1}$ ).

Lead concentrations were below the detection limit at all sites except for JF-04 and JF-05. In JF-04, lead ranged from  $<0.01 \text{ mg l}^{-1}$  to  $0.09 \text{ mg l}^{-1}$ , whereas in JF-05, it ranged from  $0.12$  to  $0.35 \text{ mg l}^{-1}$ . Sample JF-04 is of special concern because it is occasionally used as a domestic water supply, and in five of the six sampling periods it exceeded the MDWG ( $0.01 \text{ mg l}^{-1}$ ) by a factor of  $5.1$ – $8.9$ . Although JF-05 samples contained elevated levels of Pb, they did not exceed the MGIDW ( $2.0 \text{ mg l}^{-1}$ ).

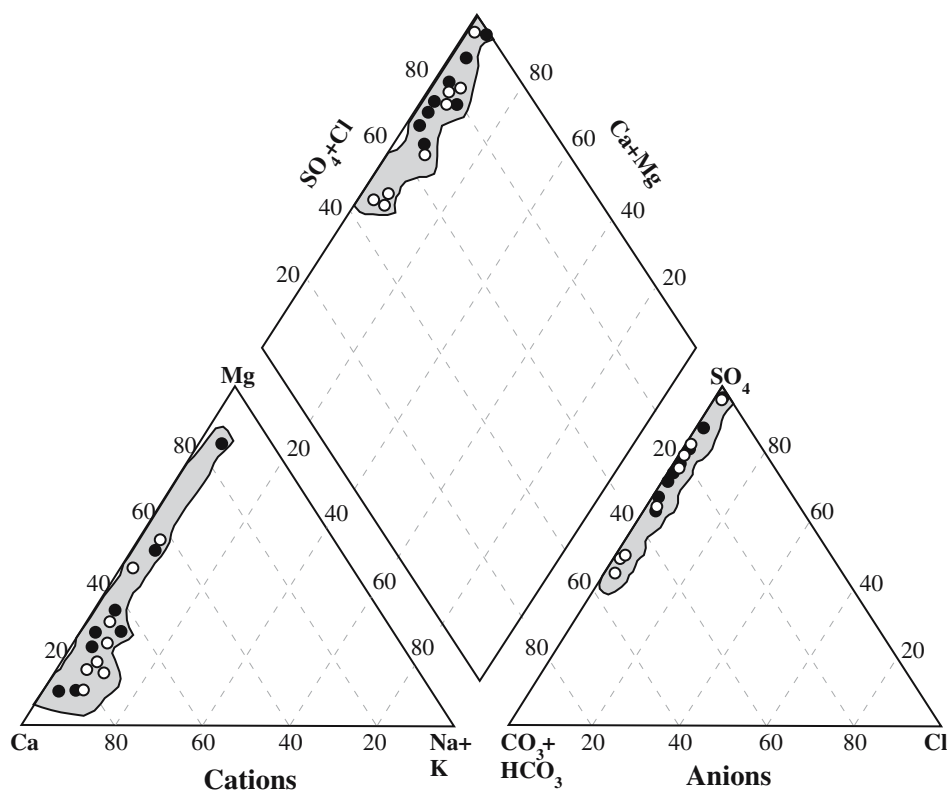


Fig. 3. Piper diagram of the studied leachates. Filled and open circles correspond to the second and fifth sampling periods, respectively.

Iron content was highly variable in the leachate samples. At near-neutral sites, Fe ranged from 0.02 to 17.5 mg l<sup>-1</sup>, whereas at the acidic site Fe ranged from 402 to 2352 mg l<sup>-1</sup>. Seasonal variation in Fe among the sites was not consistent (Figure 4a). Sites JF-02, JF-03 and JF-04 showed little seasonal variation, site JF-01 and JF-08 showed significant Fe enrichment at the end of the rainy periods and a reduction in Fe during the dry period, while site JF-06 exhibited the highest Fe concentrations during the dry period. The JF-01, JF-04 and JF-08 sites, used as domestic water sources, exceeded the MDWG (0.3 mg l<sup>-1</sup>) by a factor of 5–53. Site JF-03, which is also sometimes used as a domestic water source, only slightly exceeded the guideline during the third and sixth sampling periods.

Manganese concentrations ranged from 0.1 to 2.4 mg l<sup>-1</sup> at the near-neutral sites to values of 100–732 mg l<sup>-1</sup> at the acidic site. Seasonal changes within each site followed different patterns (Figure 4b). Sites JF-02 and JF-04 showed little seasonal change, whereas site JF-03 showed a rather chaotic pattern; the remaining sites exhibited the highest Mn concentrations during the dry season. All sites used as tap water exceeded the MDWG (0.15 mg/l) for all sampling periods by a factor ranging from 1.2 to 15.5.

Zinc content was moderately low at the near-neutral sites (<0.025–4.5 mg l<sup>-1</sup>), while at the acidic site it ranged from 104 to 1,465 mg l<sup>-1</sup>. All sites exhibited important seasonal variations (Figure 4c). For most sites the highest Zn concentrations were measured during the dry season and at the beginning of the wet period. The exceptions were sites JF-01 and JF-07, which showed the highest Zn concentration at the end of the rainy periods. All sites used as tap water were below the MDWG for Zn (5.0 mg l<sup>-1</sup>).

Arsenic concentrations were variable but generally high at the near-neutral sites, ranging from <0.010 to 1.3 mg l<sup>-1</sup>. At the acidic site, measured As ranged from 10 to 12 mg l<sup>-1</sup>. With the exception of sample JF-06, which exhibited important seasonal variations (Figure 4d), all sites showed little seasonal variation, with the highest As concentrations measured at the beginning or the end of the rainy periods (JF-01 and JF-04) or during the dry period (JF-06, JF-07 and JF-08). Three of the four sites that serve as a source of domestic water (JF-01, JF-04 and JF-08) exceeded the As MDWG (0.035 mg l<sup>-1</sup>) by a factor ranging from 1.5 to 36.3. Site JF-03 As concentrations were below the guideline. Arsenic is also considered in the MGIDW (1.0 mg l<sup>-1</sup>). Only the acidic site exceeded this guideline – by a factor of 10–12.

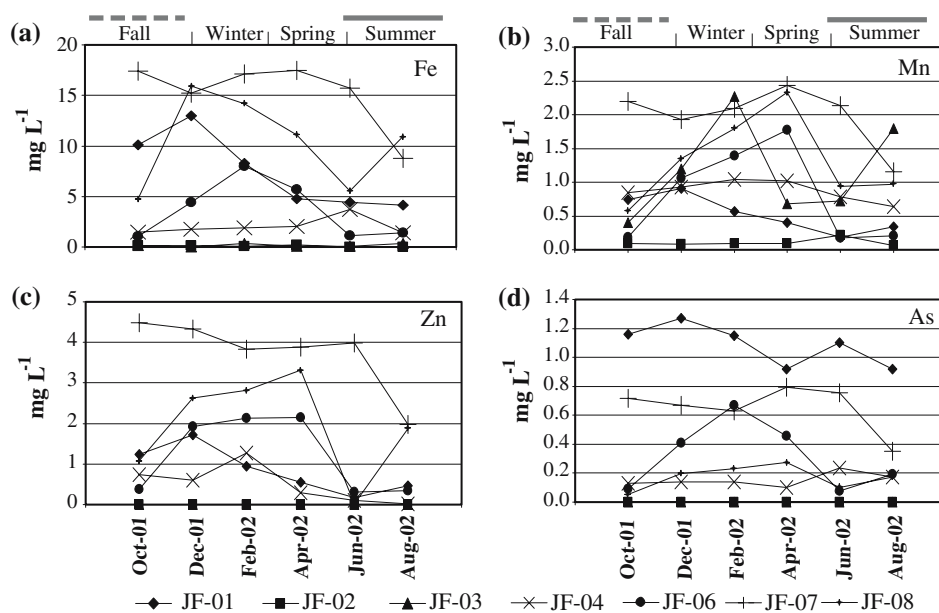


Fig. 4. Seasonal variations in the concentrations of selected trace metals in leachates from El Fraile tailings, Taxco, Mexico.



*Speciation and the saturation index*

Speciation and saturation indices (SI) were calculated for all sites for selected sampling periods (second to the fifth) using the PHREEQC equilibrium model (Pankhurst 1995) with the WATEQ4F database (Ball and Nordstrom 1991). Modeling indicates that in near-neutral samples, dissolved metals exist mainly in the form of free divalent ions ( $M^{2+}$ ), sulfates ( $M^{2+}SO_4$ ) and bicarbonates ( $M^{2+}HCO_3$ ). This speciation is typical of mining environments and has been reported in other near-neutral mine and tailings drainages (Lee & Lee 2001; Lee 2003). In acidic samples, speciation is slightly different because of low alkalinity, and chemical species exist mainly as  $M^{2+}SO_4$  and  $M^{2+}$ .

Figure 5 summarizes the SI of selected phases in modeled samples. In this figure, iron oxides (hematite, magnetite, maghemite), hydroxides (goethite) and complex Fe-hydroxichlorides [ $Fe(OH)_{2.7}Cl_{0.3}$ ] appear as oversaturated phases in the vast majority of samples, including the acidic samples. CuprosFerrite and CupricFerrite are rare Cu-Fe oxides ( $CuFeO_2$  and  $CuFe_2O_4$ , respectively) and seem to control Fe and Cu concentra-

tions in the acidic samples, appearing as oversaturated phases. Aragonite, barite, calcite, dolomite, gypsum, magnesite, rhodochrosite and siderite are oversaturated in some samples, which may lead to their precipitation. In other samples, these minerals are near-equilibrium, suggesting that small changes in physical conditions could cause precipitation or dissolution. Thus, these minerals may be the reactive solid phases controlling the concentrations of Ca, Ba, Mg and, to a lesser degree, Fe and Mn (Woo *et al.*, 2002). Other Fe phases such as  $Fe_3(OH)_8$  and amorphous  $Fe(OH)_3$  exhibit different behavior. In some samples they appear as slightly oversaturated but in other samples they are largely undersaturated. This contrasting behavior was observed in samples taken from the same site but at different times, suggesting that their saturation and solubility products are highly sensitive to slight changes in physico-chemical (e.g. temperature, pH, redox potential) conditions. Cerrusite appears as the main Pb-controlling phase in near-neutral samples with elevated Pb concentrations, whereas anglesite is the main Pb-controlling phase in acidic samples. Barium arsenate [ $Ba_3(AsO_4)_2$ ] appears as the only oversaturated As-phase in both near-neutral and

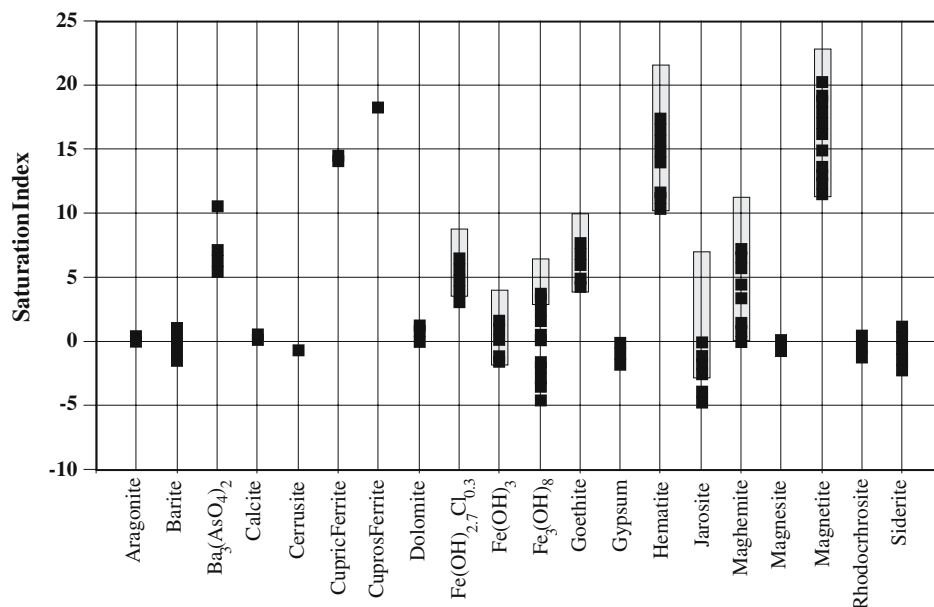


Fig. 5. Saturation index of selected phases in leachates from El Fraile tailings. *Black squares* correspond to measured conditions. *Gray fields* correspond to the saturation index calculated by adding Si and Al to the system and fixing pH = 6.7 and Eh = 0.350 V to simulate neutralization by bedrock and equilibration with atmospheric oxygen.

acid samples and seems to be the As-reactive phase in El Fraile leachates. This scenario is consistent with the pH-Eh speciation diagram for As in the presence of sulfur species determined by Drever (1997; Figure 6). This diagram shows that in El Fraile leachates, As appears primarily in the oxidized As<sup>(V)</sup> form, as  $\text{H}_2\text{AsO}_4^-$  and  $\text{H}_2\text{AsO}_4^{2-}$  in the near-neutral samples, and as  $\text{H}_2\text{AsO}_4^-$  in the acid leachates.

In order to predict the chemical phases that would exist in the presence of Si and Al and to determine changes in leachates during neutralization and equilibration with atmospheric oxygen, we recalculated the SI by fixing the following parameters: Si ( $15 \text{ mg l}^{-1}$ ), Al ( $0.050 \text{ mg l}^{-1}$ ), pH (6.7), and Eh (0.340 V). These

parameters are similar to those recorded in surface waters in the region that are not affected by mining (Bahena-Pita 2003). This analysis showed little or no change in the SI values of most phases with the exception of Fe phases for which the SI increased substantially and jarosite which became a saturated phase in most samples (Figure 5). In addition, quartz and other silica polymorphs (chalcedony) became saturated phases near the equilibrium in most samples. The most interesting change under these conditions was the great number of Al phases that became saturated or near-saturated, which includes different kinds of Al hydroxides, (Ca, K, Al) silicates, and clays (montmorillonite, kaolinite, illite and sepiolite).

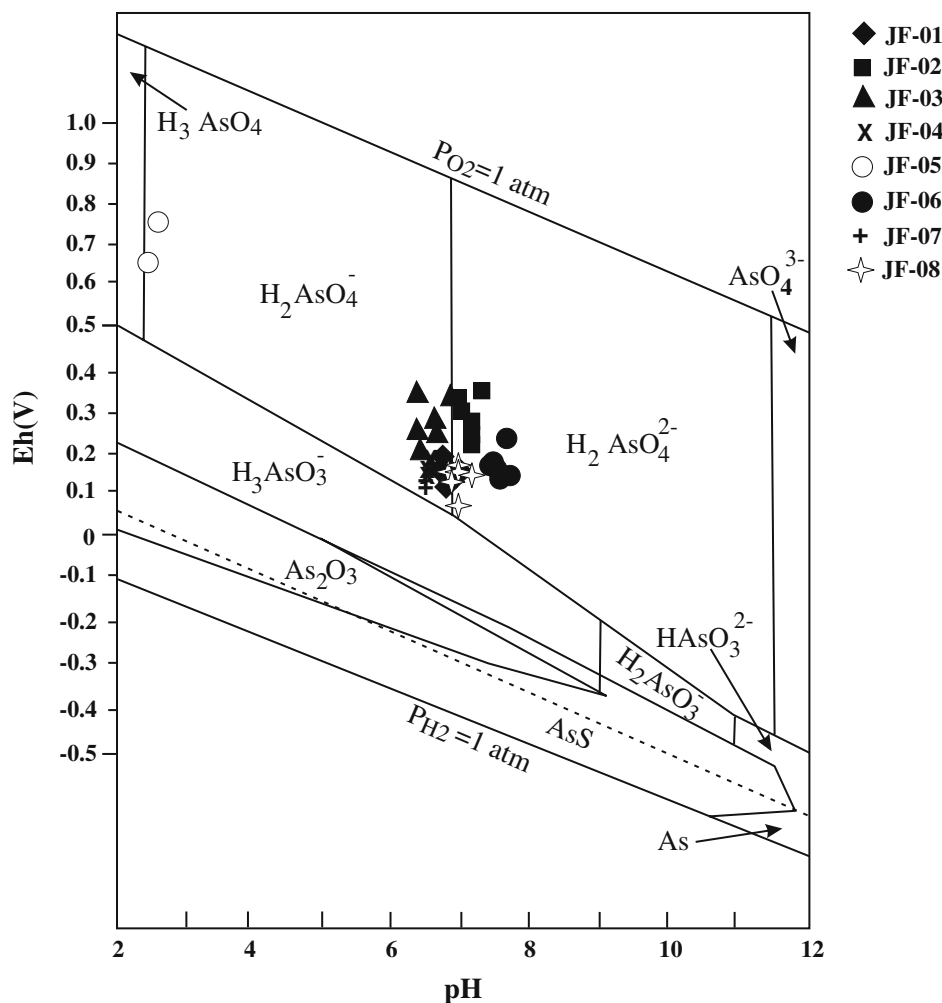


Fig. 6. pH-Eh speciation diagram for arsenic species after Drever (1997) showing the distribution of leachates from the El Fraile tailings.

## Discussion

The generation of acid mine drainage (AMD) and toxic metal-rich leachates is a major environmental problem in sulfide mining regions worldwide. In areas where tailings are located near or within communities, this problem becomes a matter of public health concern, particularly if leachates are used as a part of the domestic water supply. At such sites, the understanding of processes that influence metal release and mobility and that may exercise control on chemical speciation is an important issue for an effective environmental and health assessment.

In the El Fraile impoundment, different types of acidic and near-neutral leachates were identified. These leachates are generated by the interaction of meteoric (surface) water with tailings and bedrock (calcareous shale and sandstone). In general, there exists a tendency of leachates to contain lower metal and  $\text{SO}_4^{2-}$  and higher  $\text{HCO}_3^-$  in samples taken near bedrock than in samples taken farther away. The exception is site JF-01, which is near bedrock but which contains some of the higher measured metal concentrations. As stated earlier, bedrock is calcareous shale and sandstone containing high contents of carbonates. According to Jambor & Owens (1993), carbonate minerals are the main phases controlling acidity in leachates favoring the precipitation of secondary minerals, which in turn decreases the metal and  $\text{SO}_4^{2-}$  content and increases the  $\text{HCO}_3^-$  content. Thus, the differences measured in the chemical parameters and major and trace elements in the two types of leachate (associated or not associated with bedrock) may be related to the buffering capacity of the associated bedrock and indicates the relevance of its role to leachate chemistry. Accordingly, the  $\text{Ca}-(\text{HCO}_3 + \text{SO}_4)$  water type should be observed in leachates that have a greater interaction with carbonate bedrock, whereas  $\text{Ca-SO}_4$ ,  $(\text{Ca} + \text{Mg})\text{-SO}_4$  and  $\text{Mg-SO}_4$  water types should be observed in leachates that have a greater interaction with tailings.

El Fraile leachates were generally characterized by low concentrations of Ag, Co, V, Sb, Mo and Se. However, the levels of Pb, Cu and Cd were above the detection limit for samples taken from the acidic site, JF-05. The level of lead was also elevated in one near-neutral site (JF-04). Arsenic was above the detection limit in most samples,

while Fe, Mn and Zn were well above the detection limit in all samples. Of the elements just discussed, Co, V, Sb, Mo and Se have been found to be present at very low concentrations in El Fraile tailings (Flores-Mundo 2002; Talavera-Mendoza *et al.* 2005) and, hence, the low levels in the leachate samples was expected. In contrast, Cu, Cd, Pb, As, Fe, Mn and Zn are present in high concentrations in the tailings. These metals are soluble under highly acidic ( $\text{pH} < 3.0$ ) and oxidized conditions, which helps explain the high concentrations recorded in JF-05, the acidic samples. At slightly acidic to near-neutral pH (5.5–8.0) and under oxidized conditions, these metals precipitate to form several kinds of sulfates, carbonates and hydroxides or they are sorbed onto Fe oxides and oxyhydroxides surfaces (Peacey & Yanful 2003). The SI of the leachates studied shows that Fe oxides and Fe oxyhydroxides are oversaturated phases in many samples (Figure 5), suggesting that precipitation might occur (Drever 1997; Langmuir 1997; Hudson-Edwards 2003). When neutralization and equilibrium with atmospheric oxygen is simulated, and Si and Al are added to the system, jarosite and several kinds of clay minerals (kaolinite, montmorillonite, illite and sepiolite) become additional oversaturated phases in most leachates. Some phases like aragonite, barite, calcite, dolomite, gypsum, magnesite, rhodochrosite and siderite are near equilibrium in all samples. According to Talavera Mendoza *et al.* (2005), magnetite, hematite, bernalite, jarosite, calcite, gypsum, basanite and smithsonite as well as some evaporative phases (rozenite, epsomite) and clay minerals (kaolinite, montmorillonite, illite and saponite) have been identified at or near some of the sampling sites, thereby proving that precipitation has in fact occurred. Energy dispersive X-ray analyses performed by these authors on Fe oxides and oxyhydroxides showed that they contain appreciable amounts of Pb, Cu, Cd, As and Zn, probably as adsorbed elements. Manganese is also abundant in these phases, probably not as an adsorbed metal, but replacing Fe in the lattice structure. These results suggest that (1) the precipitation of Fe oxides and oxyhydroxides is the most important process removing Fe and Mn from El Fraile leachates; (2) adsorption may be a major process controlling the concentration of Ag, Pb, Cd, As and Zn; (3) the precipitation of jarosite would account for the further removal of Ag and

Pb from leachates, particularly when neutralized and equilibrated with atmospheric oxygen. These processes are common and have been reported in mining and smelter environments (see Nordstrom 1982; Förstner 1983; Johnson 1986; Howell 1994; Lee *et al.*, 2002).

Some of these leachates are occasionally used as a domestic water supply by the local community, particularly during dry seasons. The high leachate concentrations recorded for some metals (Fe, Mn and Pb) and As, which are well above the MDWG, represent a potential health risk for inhabitants. Seasonal behavior indicates that the levels of some metal and anions significantly increase during the dry (winter–spring) seasons, a period when leachates are more frequently used for domestic usage.

The presence of dissolved metals in most of the leachates studied suggests the potential for El Fraile tailings to release metals to the environment. The high metal content measured in the acid site samples indicates that significant amounts of metals are mobilized from tailings by a simple interaction with meteoric water during rainfall events. However, subsequent precipitation and adsorption processes considerably reduce the metal load from leachates. Near-neutral leachates contain lower concentrations of metals, but they are still high enough to be an easily available source of toxic metal. Secondary phases are generally small in size, generally  $< 100 \mu\text{m}$  (Dold 1999; Dold and Fontboté 2002), which facilitates their transport to streams and rivers as suspended particulates. These particulates can then be incorporated into bottom sediments, thereby increasing sediment metal concentrations. A study carried out by Castro de Dios (2001) on sediments from the Cacalotenango creek showed that sediments are highly enriched in Fe, As, Pb, Cu, Zn and Cd even as far as 10 km away from the emission point. It has been established that metals sorbed onto Fe oxyhydroxides are highly sensitive to pH/Eh changes in the water column and that metals can be easily liberated along hydraulic gradient several kilometers from the source point, consequently becoming a permanent source of toxic metals (Jambor and Owens 1993).

### Conclusion

Leachates from the El Fraile impoundment in Taxco, Mexico are acidic to near-neutral solutions

that are generated by varying degrees of interaction between the surface water and both tailings and bedrock. These leachates are sometimes used as alternative sources of domestic water by inhabitants. They have physical and chemical characteristics of the Ca–(HCO<sub>3</sub> + SO<sub>4</sub>), Ca–SO<sub>4</sub>, (Ca + Mg)–SO<sub>4</sub> and Mg–SO<sub>4</sub> water types typical of mining environments.

El Fraile leachates are characterized by high contents of SO<sub>4</sub><sup>2-</sup>, Fe, Mn, Zn and Pb, with the highest metal enrichment occurring during the dry seasons. Leachates used as domestic water typically exceed the Mexican Drinking Water Guidelines for sulfate, hardness, Fe, Mn, Pb, and As and represent a potential public health risk to inhabitants. Acidic leachates exceed the Mexican Guidelines for Industrial Discharge Waters in pH, Cu, Cd, and As, thereby representing an easily available source of metals to surface water and bottom sediments.

Speciation indicated that in near-neutral solutions, metals exist mainly as free ions, sulfates and bicarbonates, and in acidic leachates they are present as sulfates and free ions. Arsenic appears as As<sup>(V)</sup> in all samples. The SI indicated that the precipitation of Fe oxides and oxyhydroxides, clay minerals and jarosite as well as sorption by these minerals are the main processes controlling leachate chemistry. These processes occur mainly after neutralization through the interaction with bedrock and equilibration with atmospheric oxygen.

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