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Geochemical behavior of heavy metals in a Zn–Pb–Cu mining area in the State of Mexico (central Mexico)

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Abstract The geochemical behavior of zinc, lead and copper from sulfidic tailings in a mine site with potential to generate acidic drainage (pyrite (55%) and sphalerite (2%)) is reported in this paper. The mining area is divided in two zones, considering the topographic location of sampling points with respect to the tailings pile: (a) outer zone, out of the probable influence of acid mine drainage (AMD) pollution, and (b) inner zone, probably influenced by AMD pollution. Maximum total ions concentrations (mg/L) measured in superficial waters found were, in the outer zone: As (0.2), Cd (0.9), Fe (19), Mn (39), Pb (5.02), SO_4^{2-} (4650), Zn (107.67), and in the inner zone are As (0.1), Cd (0.2), Fe (88), Mn (13), Pb (6), SO_4^{2-} (4,880), Zn (46). The presence of these ions that exceeding the permissible maximum limits for human consume, could be associated to tailings mineralogy and acid leachates generated in tailings pile.

Keywords AMD · Heavy metals · Massive sulfide · Tailings · Superficial water pollution

Introduction

The pollution caused by heavy metals is a long term, irreversible process. Usually, the natural contamination by heavy metals originates from the weathering of minerals and rocks in aquatic environments. Extraction of metals from sulfide ores commonly results in 90% of the minerals being discarded as tailings (Moore and Luoma 1990). Rivers and other superficial waters, as well

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as soils located near operating and abandoned sulfide ore mines, are often affected by acid runoff from mine workings, tailings, and waste rock piles (Boularbah et al. 2006; Lee et al. 2005). This phenomenon is known as acid mine drainage (AMD), a common type of pollution in mining sites, which results from the oxidation of sulfides, mainly pyrite (Rojas and Vandecasteele 2007). Tailings and associated overburden materials often contain elevated concentrations of metals (Cu, Zn, Cd, and Pb) and are a potential source of localized ground and surface water contamination. Pore water and drainage solutions from sulfide rich wastes are characterized by low pH values (2.0–3.0) and high concentrations of heavy metals, indicators of AMD contamination in mine sites (El Khalil et al. 2008; Lee et al. 2005; Levy et al. 1997).

Research on the environmental geochemistry of heavy metals has been performed all around the world with different approaches. For example, Neves and Matias (2008) and Zhou et al. (2008), among others, have considered the environmental geochemistry of one specific metal on mining sites, thallium and uranium, respectively; whereas some other authors work on the environmental geochemistry of several common AMD metals (Carrillo-Chávez et al. 2003; Ramos-Arroyo and Siebe-Grabach 2006). Authors, like Moon et al. (2008) and Salomons (1995), have focused on the potential acid-producing capacity of tailings; while others (Ghose and Majee 2007) have studied the hazardous airborne dust around coal mining areas.

In the study area, a volcanogenic massive sulfide deposit is exploited commercially. This mining region is a valuable source of metals, since the dominant mineral bodies are: zinc (7.9%), lead (1.8%), copper (0.7%), and in minor quantities, silver (325 g/t), and gold (1.9 g/t). The area had been studied with respect to the economic ore potential and the geology for prospecting, but in the last years, the environmental geochemistry perspective has also been considered (Lizárraga-Mendiola et al. 2008). The purpose of this study was to examine the geochemical composition of superficial waters around the tailings pile and its relationship with mineralogy and geochemical composition of mining wastes.

Description of the study area

The study area is located south west of the State of Mexico, near the town of San Juan Zacazonapan (Fig. 1a). The altitude is 1200 m.a.s.l., and the predominant climate is from temperate to warm with dry winter and rainy summer. During the months of July, August and September, the region receives the maximum precipitations. The annual average precipitation is 1,500 mm. The temperature in summer exceeds 30°C, and the temperature in winter oscillates from 10 to 16°C.

At the processing plant, the extracted mineral is crushed and milled to 200-mesh particle size. The zinc, lead, and copper sulfides are concentrated by flotation, and the remnant materials, around 95% of the mineral (rich in pyrite, FeS_2), are pumped as water slurry to the tailings pile. The mineralogy of these tailings present high contents of potentially acidic drainage generating minerals: Pyrite (55%), sphalerite (2%), galena (0.7%), and chalcopyrite (0.6%). Studies have been made on the generation of acid leachates of these tailings, which confirmed the potential of acid drainage generation due to its high pyrite content and the absence of neutralizing material (González-Sandoval et al. 2008). Currently, this mine site is active, the tailings pile surface area is 132800 m^2 approximately, and contains around 5.5 millions of tons of tailings.

Materials and methods

Superficial water

Water and tailing samplings were done during several years (2004–2006). During 2004, nine samples were taken, in 2005, 23 in dry (April) and humid (August and September) seasons, and five samples in 2006, during dry (March) season. All the samples were taken by duplicate. The sampling points location is shown in Fig. 1b, and their description is in Table 3. All the samples correspond to superficial waters, including sample PJMA8, since, although described as groundwater from the mine, it was monitored from superficial pools. Before sample collection (1 L approximately for each sample), acid washed bottles were rinsed with the

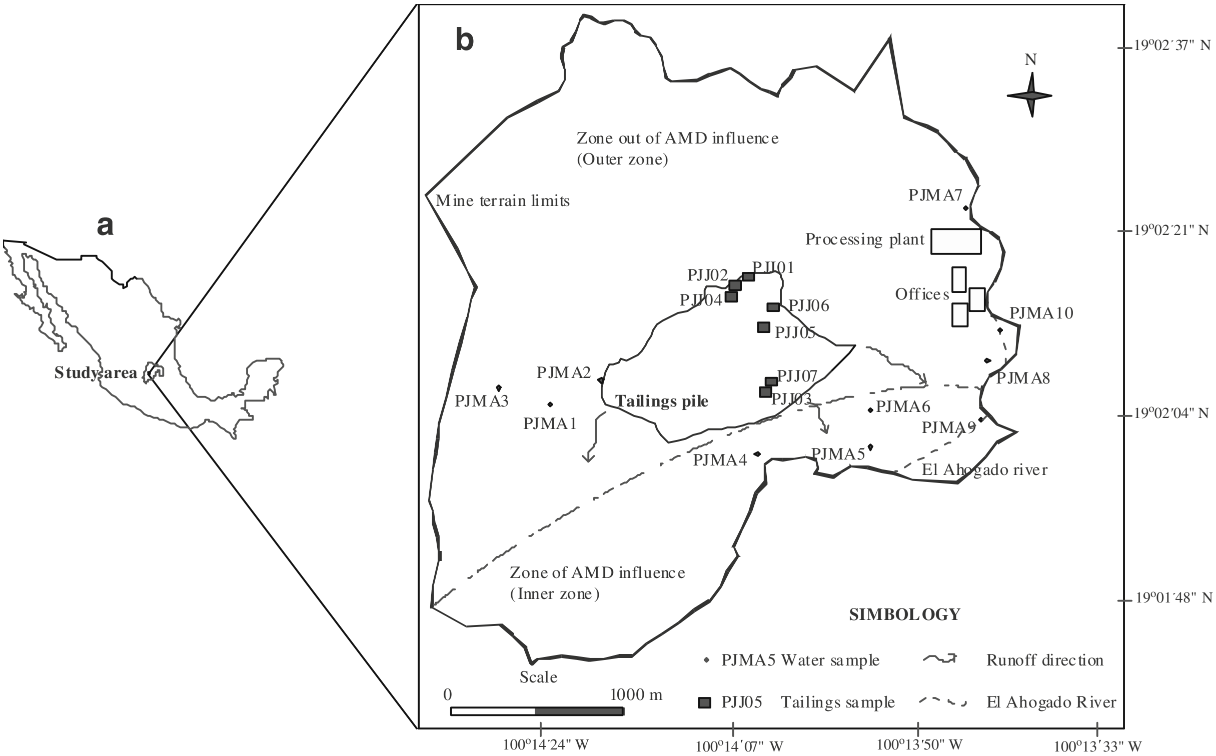

Fig. 1 Location map. **a** Location of the study area, and **b** Location of water and tailings sampling point

site water two or three times before taking the water sample.

The collected samples were measured in situ for physical parameters such as: temperature, pH, and electrical conductivity, using a Corning field equipment Model Checkmate II, according to the manual instructions. The samples were acidified with nitric acid until pH 2, and digested according to EPA method 3005A (1992) afterwards for elemental analysis (Al, As, B, Cd, Cu, Fe, Li, Pb, Mn, Si, Sr, and Zn), by Inductively Coupled Plasma with Optical Emission Spectroscopy-ICP-OES (Perkin Elmer 2002 mod. Optima 4300 DV)—in the Department of Metallurgical Chemical Engineering, Faculty of Chemistry, UNAM. Duplicates of these samples were sent for analysis to the mine laboratory for results intercalibration, using similar ICP-OES equipment. The detection limits (μg/L) of the equipment for the following elements are: Al (20), As (5), B (10), Cd (0.2), Cu (25), Fe (100), Pb (3), Mn (20), and Zn (20). Quality control was based on the use of a certified water sample (fresh water, SRLS-1: National Research Council of Canada, 2006). The digested blank (deionized water) showed a value less than detection limits. A blank and standards used for calibration were tested periodically; in order to validate the analytical work, the reference water sample was analyzed also. Samples for alkalinity and anion determinations were stored at 4°C without preservatives until their analysis, in the Faculty of Chemistry, Department of Metallurgical Chemical Engineering, UNAM.

Sulfates were quantified by triplicate according to the methodology proposed by the norm NOM-141-SEMARNAT-2003 (2004). The results obtained were compared with environmental norms (NOM-127-SSA1 1994; US National Primary Drinking Water Standards 2003) to determine their quality for human use (Tables 1 and 2). Distances from the sampling locations to the tailings pile are included in Tables 1 and 2. Accuracy of the chemical analysis was verified by calculating the ionic balance error (Hem 1970), including the certified reference material; the values obtained were lower than 10%.

Table 1 Water chemistry results obtained in samples located in the Inner Zone (units in mg/L)

Parameter	PML[a] (mg/L)	Mean	Máx	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	SRLS-1[b]
Location		PJMA4			PJMA5			PJMA6			PJMA9			
Distance (m)		150.00			400.00			350.00			1300.00			
pH	6.5–8.5	5.56	6.81	4.08	4.90	6.24	3.57	5.70	7.62	3.98	5.81	7.60	2.50	7.71
EC (μS/cm)	100	4327.50	5800.00	450.00	4457.50	6260.00	450.00	4532.50	6500.00	450.00	5221.67	8660.00	205.00	278.00
Alcalinity ($CaCO_3$)		53.00	80.00	10.00	63.75	98.00	35.00	88.25	106.00	67.00	95.00	110.00	85.00	102.00
Al		0.05	0.09	0.02	0.07	0.08	0.05	0.08	0.09	0.08	0.05	0.10	0.03	
As	0.025	0.10	0.10	0.10		0.00	0.00	0.10	0.10	0.10				
B		1.24	2.02	0.60	2.35	3.24	1.80	2.30	3.19	1.80	3.00	3.00	3.00	0.31
C		29.12	29.12	29.12	30.09	30.09	30.09	38.42	38.42	38.42				47.07
Ca		522.73	560.00	501.00	667.80	722.40	560.00	669.47	723.00	576.40	298.70	588.20	9.20	25.30
Cd	0.005	0.04	0.04	0.04	0.11	0.20	0.06	0.15	0.19	0.11				
Cl	250	69.96	109.02	50.10	107.59	186.50	47.60	171.03	235.00	96.11	229.67	245.00	216.00	10.47
Cu	1	0.09	0.09	0.09	0.04	0.05	0.02	0.04	0.04	0.03				
Fe	0.3	2.29	4.10	0.48	17.67	48.80	5.90	7.05	9.57	5.60	30.94	88.56	0.46	0.35
H		10.54	10.54	10.54	13.86	13.86	13.86	10.42	10.42	10.42				10.23
HCO_3^-		91.25	100.00	75.00	96.25	110.00	80.00	71.00	110.00	34.00				120.00
K		32.46	118.00	1.31	68.09	265.00	1.45	70.76	277.00	1.15	2.34	2.54	2.15	5.80
Li		0.18	0.27	0.13	1.72	1.98	1.58	1.60	1.69	1.49	2.06	2.06	2.06	
Mg		624.87	678.20	596.40	372.73	592.40	251.00	374.53	600.60	252.00	153.20	303.20	3.20	13.56
Mn	0.05	6.65	8.16	4.50	7.05	12.01	3.18	7.37	12.81	3.18	3.71	7.35	0.06	0.17
Na		104.78	386.00	10.00	196.60	724.40	19.50	198.26	732.00	15.65	31.73	39.00	25.70	18.70
Pb	0.01				3.62	4.60	2.98	4.28	5.60	3.44	1.47	1.47	1.47	
Si		37.76	39.27	35.02	652.29	2594.02	3.59	1120.08	3348.82	4.38	18.62	24.73	12.50	24.03
SO_4^{2-}	250	3477.56	3830.00	2883.06	3938.85	4660.00	2806.55	2659.87	4880.00	5.00	2133.63	3786.85	20.00	
Sr		3.04	3.43	2.50	2.04	2.23	1.80	2.08	2.20	1.90	1.40	2.70	0.10	0.23
Zn	5	10.71	17.80	4.06	26.40	46.20	7.42	26.60	45.60	7.13	6.58	8.15	5.00	0.48

For location of samples, see Fig. 1b

Blank spaces: Concentrations were not quantified

[a] *PML* Permissible Maximum Limits established by NOM-127-SSA1 (1994) and US National Primary Drinking Water Standards (2003)

[b] *SRLS*1 Certified Reference Material (for fresh water) from National Research Council of Canada (2006)

Table 2 Water chemistry results obtained in samples located in the Outer Zone (units in mg/L)

Parameter	PML[a] (mg/L)	Mean	Max	Min	Mean	Max	Min		Mean	Max	Min	Mean	Max	Min		SRLS-1[b]
Location		PJMA1			PJMA2			PJMA3	PJMA7			PJMA8			PJMA10	
Distance (m)		250.00			50.00			700.00	1500.00			1000.00			950.00	
pH	6.5–8.5	7.91	8.76	7.27	7.43	9.35	5.19	6.73	7.21	7.54	6.90	5.40	6.20	3.54	7.79	7.70
EC (µS/cm)	100	103.13	132.10	79.60	90.97	94.30	85.70	120.70	146.43	152.30	141.00	4337.25	6250.00	749.00	205	352.00
Alcalinity ($CaCO_3$)		92.00	110.00	76.00	51.00	83.00	25.00	106.00	99.33	100.00	98.00	100.00	100.00	100.00	98	106.00
Al		0.26	0.40	0.05	0.03	0.05	0.02	0.02	0.04	0.04	0.04	0.04	0.06	0.02		
As	0.025				0.10	0.10	0.10					0.20	0.20	0.20		
B									0.33	0.33	0.33	3.43	4.10	3.10		0.27
C									34.45	34.45	34.45	28.56	34.45	16.78		23.08
Ca		14.90	20.20	9.60	6.80	7.80	5.80	9.40	11.75	13.80	9.70	440.27	723.80	296.00		56.60
Cd	0.005											0.63	0.90	0.36		
Cl	250	64.67	77.00	52.00	63.07	78.00	53.20	48.30	136.82	242.00	4.45	194.07	236.00	98.26	245	7.03
Cu	1	0.03	0.03	0.03								0.12	0.16	0.07		
Fe	0.3	1.98	4.20	0.54	2.53	5.20	0.46	5.13	2.02	4.00	0.03	9.86	18.80	5.10	3.4	0.05
H									14.44	14.44	14.44	16.34	16.34	16.34		14.56
HCO_3^-									120.00	120.00	120.00				900	130.00
K		1.99	2.43	1.23	1.76	2.51	1.15	1.62	2.53	3.30	2.11	70.37	274.00	1.85	2.92	4.50
Li								0.02				1.78	2.15	1.58		
Mg		3.90	4.80	3.00	4.20	4.40	4.00	5.80	10.68	10.80	10.56	554.07	607.20	484.60		8.79
Mn	0.05	0.04	0.05	0.03	0.05	0.05	0.04	0.26	0.03	0.03	0.03	13.16	15.20	11.50	39.5	
Na		3.10	4.30	2.50	6.29	10.00	4.33	10.50	24.93	33.60	11.00	215.63	762.40	27.50		14.40
Pb	0.01											1.92	5.02	0.13		
Si		3.50	5.02	1.97	6.79	7.60	5.97	9.99	27.71	28.67	26.75	13.70	17.56	6.24	20	14.85
SO_4^{2-}	250	10.93	11.39	10.47	11.88	11.88	11.88	21.12	20.74	20.74	20.74	3506.99	4650.00	2216.39		
Sr		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.12	0.13	0.10	1.92	2.57	1.50		0.36
Zn	5	2.70	4.99	0.62	2.92	5.08	1.27	7.46	1.73	4.81	0.07	67.60	107.67	37.50	4.15	0.06

For location of samples, see Fig. 1b

Blank spaces: Concentrations were not quantified

[a] *PML* Permissible Maximum Limits established by NOM-127-SSA1 (1994) and US National Primary Drinking Water Standards (2003)

[b] *SRLS*1 Certified Reference Material (for fresh water) from National Research Council of Canada (2006)

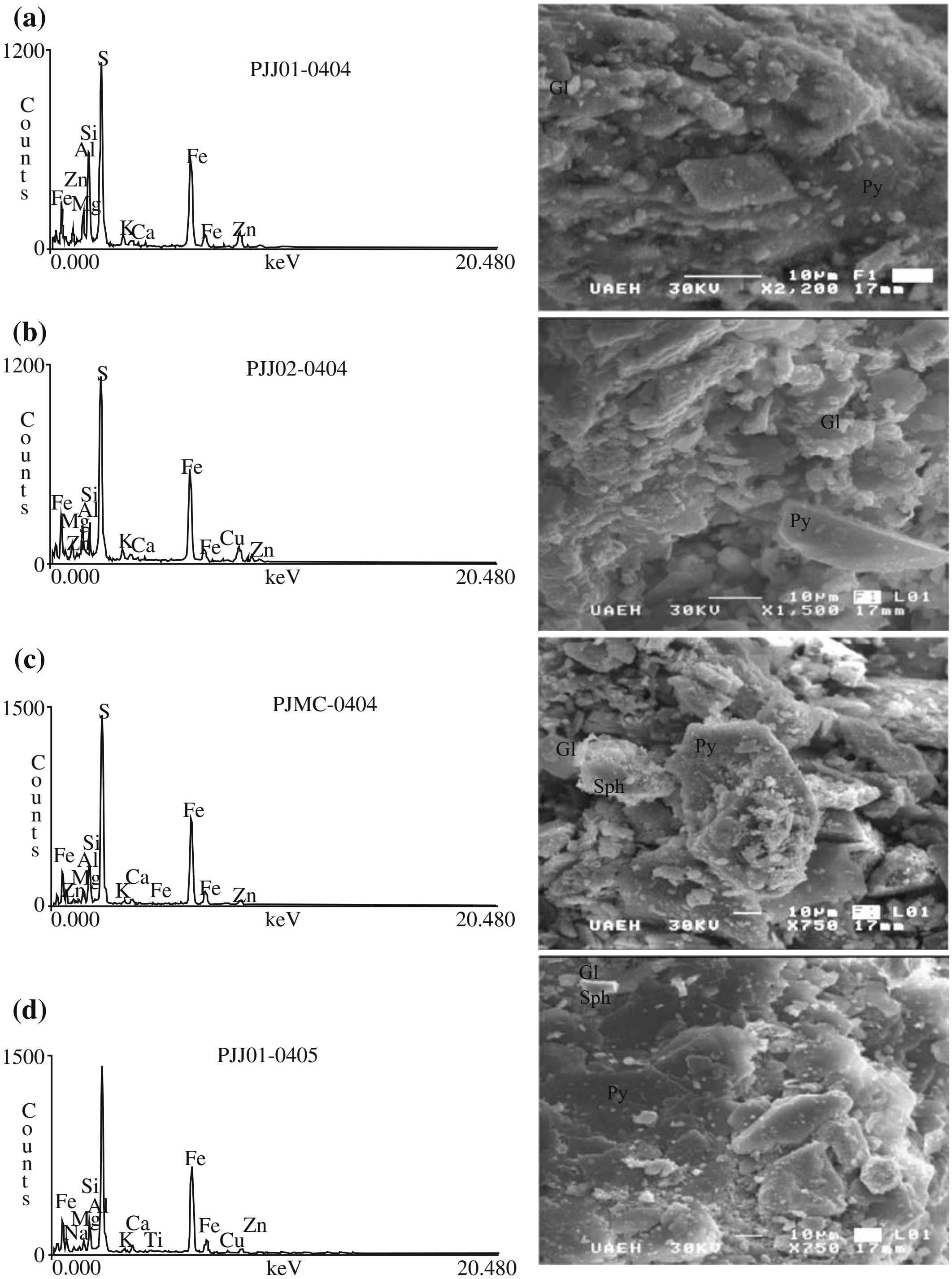

Fig. 2 **a** to **d**. EDS microanalysis of tailings samples. Microphotographs represent predominant mineral morphology. *GI* Galena, *Py* pyrite, *Sph* sphalerite. *PJMC-0404* PJJ01, PJJ02 and PJJ03. 0404 April 2004, 0405 April 2005. **e** to **g**, EDS microanalysis of tailings samples. Microphotographs represent predominant mineral morphology. *Gl* Galena, *Py* pyrite, *Sph* sphalerite. See location in Fig. 1b. 0405 April 2005, 0805 August 2005

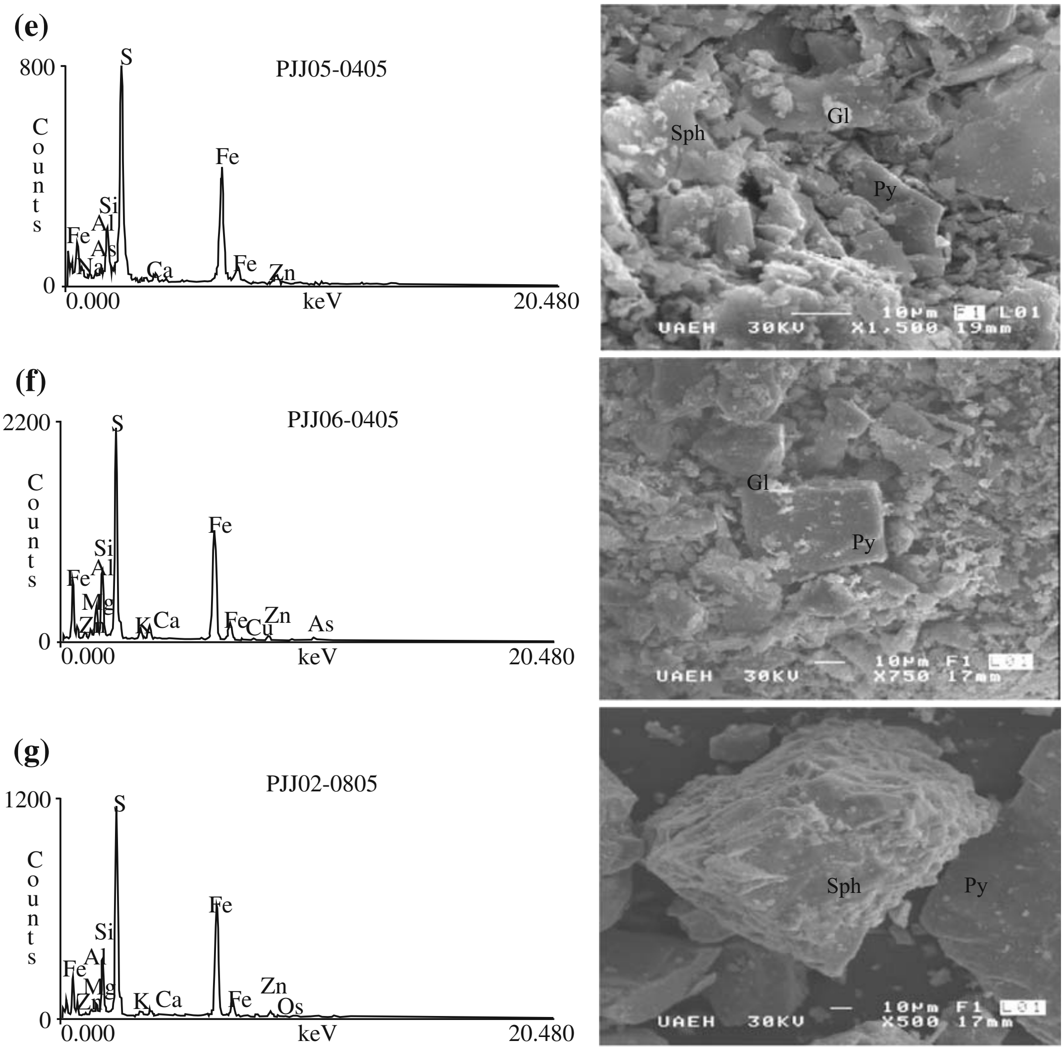

Fig. 2 (continued)

The study area was divided in two zones, inner and outer zone, as indicated in Fig. 1b. This division was done according to the following criteria: All sampling points located in the inner zone (PJMA4, PJMA5, PJMA6, and PJMA9, south and southeast), are located downstream the tailings pile, with respect to the local topography. On the other hand, all the sampling points in the outer zone (PJMA1, PJMA2, PJMA3, PJMA7, PJMA8, and PJMA9, western, and northeastern), are located upstream or at the same level of the tailings pile, according to the local topography. Therefore, there is more probability that superficial water bodies located in the inner zone can be affected by the AMD originated in the tailings pile, due to natural runoff orientation.

Hydrogeochemical modeling

Speciation is a calculation of the equilibrium distribution of mass among complexes and redox couples (Parkhurst and Appelo 1999). The saturation index (SI) is defined as: $SI = \log(IAP / K_{sp})$, where IAP is ion activity product and K_{sp} is the solubility product for a given temperature. This means that when $IAP = K_{sp}$, then $SI = 1$, and water is at thermodynamic equilibrium with respect to the mineral. When $SI > 1$, water is supersaturated with respect to the mineral and can precipitate. On the other hand, if $SI < 1$, water is undersaturated with respect to the mineral and it should dissolve. PHREEQC was the hydrogeochemical modeling program used, and has the capability to handle environmental pollution problems (Table 4). Wateq4f was the database included in the modeling program utilized for the hydrogeochemical calculations (Parkhurst and Appelo 1999).

Tailings

Tailings mineralogical composition was determined through a semi-quantitative analysis by X Ray diffraction (XRD), and described previously by Lizárraga-Mendiola et al. (2008). Another technique used to determine the quantitative mineralogical and chemical composition of tailings was the Energy Dispersive Spectrometer (EDS-X ray microanalysis), using the X-ray dispersive energy technique (Table 5, Fig. 2a–g).

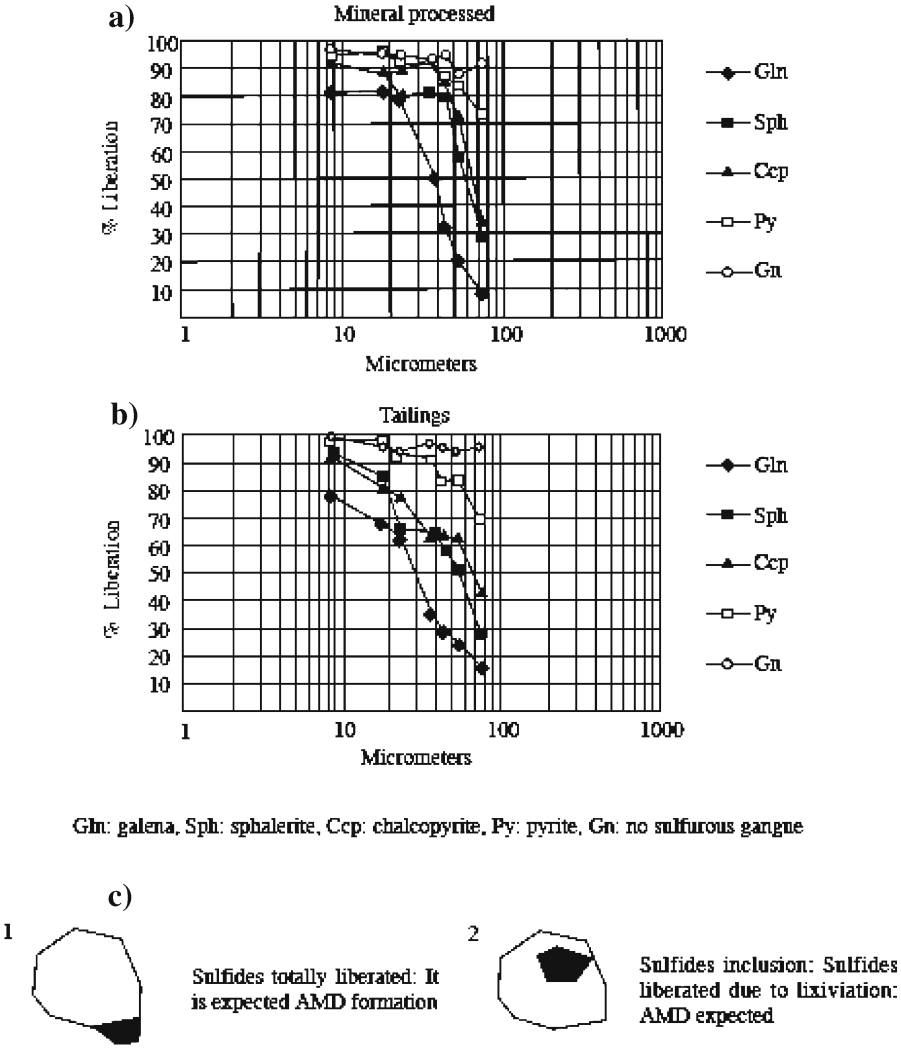

Fig. 3 **a** to **c** Mineral liberation. **a** Mineral liberation from mineral processed, **b** mineral liberation from tailings, and **c** mechanisms of mineral liberation

The equipment used was a Thermo Electron JEOL Mod. JSM-6300 microscope (Scanning Microscope WDS/EDS System), with morphological observation of high resolution (3.0–4.0 nm), capable to detect elements from Na to U. This analysis was performed at the Department of Scanning Electron Microscopy, academic area of Materials and Metallurgy, UAEH.

Another technique used to determine the mineralogical characteristics of grains is a modal analysis through the optical polarized light microscopy and particles counting. Each sample was fractioned in a Warman Cyclosizer in ranges from 1 to 100 μm. The modal analysis consists in the observation through microscope and the record of a statistical number of mineral particles in a crushed sample. The objective of this modal analysis involves determining the relative proportions of liberated particles for each mineral species in the head mineral (before being processed) and in tailing samples, which were done in the mine laboratory (Fig. 3a, b, c).

Results and discussion

Water chemistry

From Tables 1 and 2, the chemistry of superficial water bodies in the study area was divided in two zones. Description of each sampling location is included in Table 3. These are based on the location of the sampling points with respect to the tailings pile and their topographical position (Fig. 1b): (1) zone of influence of AMD contamination (inner zone) at the south and southeastern part of the tailings pile, where the sampling points PJMA4, PJMA5, PJMA6, and PJMA9 were characterized, and (2) zone out of influence of AMD contamination (outer zone) at the west and northeastern part of the tailings pile, where the sampling points PJMA1, PJMA2, PJMA3, PJMA7, PJMA8, and PJMA10 were characterized. In these two zones, some elements that exceeded the permissible maximum limits (PML) established by the environmental norms (NOM-127-SSA1-1994 1994, and US National Primary Drinking Water Standards 2003) for human consume (Tables 1 and 2). Considering there exists a river crossing near to the tailings pile (sampling points PJMA9 and PJMA10 through El Ahogado river), population located downstream this mining site could be affected after consuming this water.

Inner zone

Table 1 gives ranges of the physical characteristics and the concentrations of metals in all superficial water bodies analyzed in this zone. The lowest pH value was 2.5 (PJMA9, El Ahogado river, downstream), whereas the highest pH value was 7.62 (in PJMA6, tailings water deviated through pipes). The medium to high electrical conductivity (205–8,660 μS/cm) reflects medium to high content of dissolved ions. The highest concentration of these ions and distances from tailings pile were distributed as follows (units are in mg/L): In PJMA4, 140 m south (As = 0.1, Cu = 0.09, Mg = 678, and Sr = 3; this was the only sampling point where

Table 3 Description of water samples

Water sample	Description (distance from tailings pile in m)
PJMA1	Small pond located (250 m) to the west of tailings pile
PJMA2	Small pond located (50 m) to the west of tailings pile
PJMA3	Small pond located (700 m) to the west of tailings pile
PJMA4	Rain water deviated (150 m) before reaching the tailings pile
PJMA5	Water recovered (400 m) from processing activities
PJMA6	Tailings water deviated through pipes (350 m) (used for reprocessing activities)
PJMA7	Spring water (1,500 m; conducted through pipes; considered superficial water sample)
PJMA8	Groundwater from mine activities deposited as superficial water in pools (1000 m)
PJMA9	El Ahogado river (1,300 m) downstream from tailings pile
PJMA10	El Ahogado river (950 m) upstream from tailings pile

See Fig. 1b for location

Pb was not quantified); in PJMA5, 400 m south (B = 3, Cd = 0.2, HCO_3^- = 110, and Zn = 46); in PJMA6, 350 m southeast (As = 0.01, HCO_3^- = 110, Mn = 13, Na = 732, Pb = 6, Si = 3,349, and SO_4^{2-} = 4,880); in PJMA9, 1300 m El Ahogado river downstream (pH = 2.5, Al = 0.1, Cl = 245, Fe = 88, Li = 2, and CE = 8,660 μS/cm). Some of these values are of comparable magnitude as those found in mine water from Cu, Pb, and Zn producing mines in Canada: pH = 4–2, Mn = 21–0 mg/L, Pb = 58–0.4 μg/L, and Fe = 1830–79 mg/L. It was noted that these Canadian mine waters had a negative effect on aquatic ecosystems (Rojas and Vandecasteele 2007; Sengupta 1993). Other authors have reported low pH values in other mines (2–3; El Khalil et al. 2008). From this chemical composition in the study area, it has been observed that dissolved ions exceeding the permissible maximum limits (PML) for human consume were: As (four times), Cd (eight to 40 times), Fe (one to 295 times), Mn (one to 256 times), Pb (147–560 times), SO_4^{2-} (19.5 times), and Zn (nine times), as well as EC (86 times).

Outer zone

Table 2 shows the physical and chemical results obtained in this zone. The lowest pH value was 3.5, in PJMA8, the highest pH value was 8.7, in PJMA1. Electrical conductivity shows values from low to high (79 to 6,250 μS/cm), indicating low to high content of dissolved ions. The highest concentration of these ions and distance from tailings pile was distributed as follows (values in mg/L): In PJMA1, 250 m west (Al = 0.4); in PJMA7, 1,500 m northeast (Cl = 242, Si = 29); in PJMA8, mine groundwater sampled in superficial water pools, 1,000 m east (EC = 6250 μS/cm, As = 0.2, B = 4, Ca = 724, Cd = 0.9, Cu = 0.16, Fe = 19, Li = 2, Mg = 607, Na = 762, Pb = 5, SO_4^{2-} = 4650, Sr = 3, Zn = 108); and in PJMA10, 950 m El Ahogado river upstream (HCO_3^- = 900, Mn = 39). The rest of the sampling points located in outer zone were lower than these concentrations. It has been observed that dissolved ions exceeding the permissible maximum limits (PML) for human consume were: As (four to eight times), Cd (72–180 times), Fe (ten to 63 times), Mn (790 times), Pb (13–502 times), SO_4^{2-} (19 times), and Zn (21 times), as well as EC (62 times).

Comparing the results of both zones, almost all the ions concentrations were higher in the inner zone, excepting for As, Cu and Zn, that were higher in the outer zone, and the highest SO_4^{2-} concentrations were almost the same in both zones. The low pH of PJMA8 water (3.54) was probably responsible for the high metals mobilization in this sampling point, suggesting a problem of acid mine drainage (because this is mine groundwater exposed to atmospheric conditions—or oxidation of rocks—when it is deposited in pools for its use).

Figure 4 represents the Ficklin's diagram for the results included in Tables 1 and 2. Differences in the sum of the base metals (Cd, Cu, Pb, and Zn) allow to differentiate between several geological controls that influence the composition of water (Plumlee et al. 1999). From this diagram the following observations can be mentioned: (a) in the inner zone, the base metals in the superficial runoffs are distributed from acid to near neutral environments, with high concentrations of dissolved metals, predominating an acid environment. It is necessary to mention that although this diagram does not take into account the SO_4^{2-} for not being a base metal, in Table 1 it is observed that this high concentration indicates the presence of these elements, and (b) in the outer zone, the distribution of base metals in the superficial runoffs indicates an environment from near-neutral, with high concentrations of dissolved metals, to a near-neutral with low concentrations of dissolved metals, predominating the first type. This coincides with the description quoted previously, where it is mentioned that in spite of not being in the direction of AMD migration, it is very probable that natural weathering of rocks or eolian tailings particles transportation, causes this high concentration of certain metals typical of AMD (Fe, Zn, Mn, and Pb), without being very harmful to the water quality. It is possible that the chemical composition of these water bodies is influenced by the local geology (where volcanogenic massive sulfide deposit predominates), since, although it does not show indications of acidic drainage, the presence of Mn and Fe can

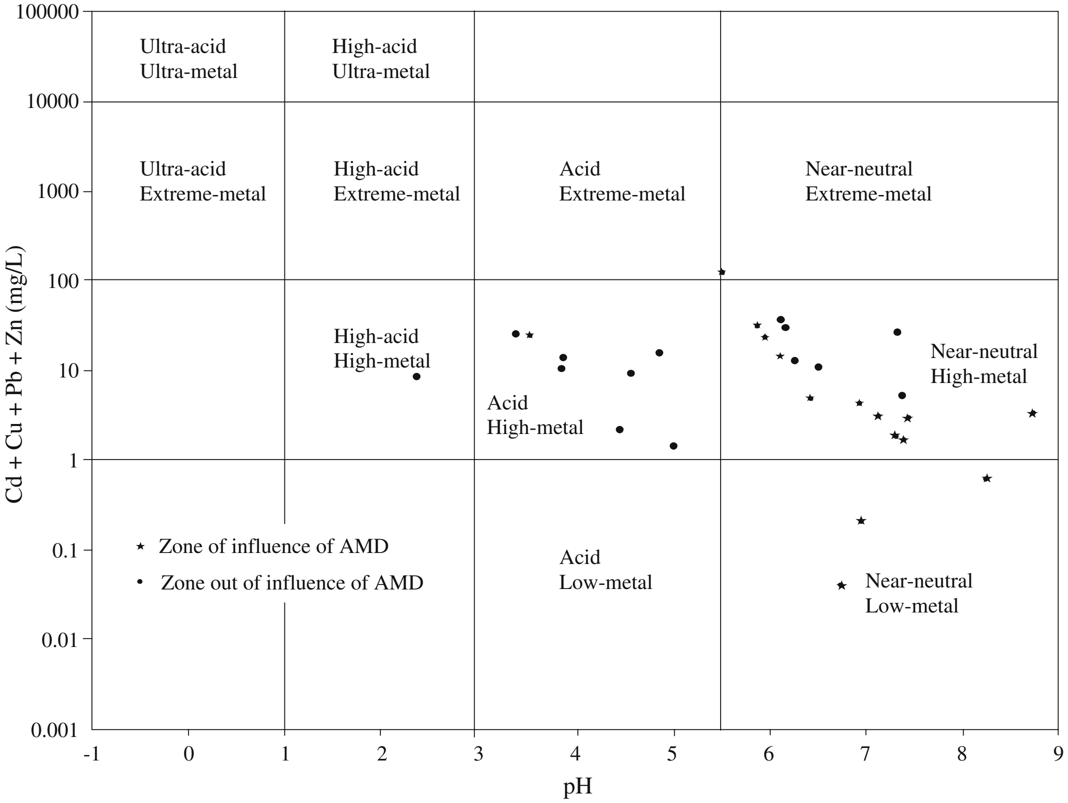

Fig. 4 Base metal environments, based on Ficklin's diagram (From Plumlee et al. 1999)

be due to the natural weathering of rocks (rich in iron). Ingri et al. (1997) observed that dissolved Fe and Mn concentrations could be related with former low dissolved O_2 concentrations in mine water and bottom lakes water.

The relationship among sampling points distances to tailings pile and the maximum metals concentration was compared. In the inner zone (Fig. 5a), metals such as Cd and Fe were in lower concentrations at short distances from the tailings pile (PJMA4, 150 m), and this was the only sampling point with no Pb concentration detected. At medium distances sampled (PJMA6, 350 m and PJMA5, 400 m), Cd, Mn, Pb, and Zn were quantified in higher concentrations. The waters from these sampling points are recirculated to the concentration process, and it is possible that this chemical behavior is due to direct contact with minerals exploited in the mine. On the other hand, long distance superficial water body sampled (PJMA9, 1,300 m) showed low concentrations of all these ions, except for Fe, which is the only metal quantified in higher concentrations in this sampling point. This could indicate that although AMD is influencing the inner zone, natural weathering and eolian tailings particle transportation can also contribute to increase iron concentrations. From Fig. 5b, Cd and Pb were quantified only in PJMA8 (1,000 m). At short distances (PJMA1, 250 m; PJMA2, 50 m, PJMA3, 700 m), Mn was in lower concentration, it was not detected in PJMA7 (1500 m), and was in higher concentrations at long distance (PJMA10, 950 m). Fe was in its lowest concentration at long distance (PJMA7, 1500 m and PJMA10, 950 m) and highest in PJMA8 (1,000 m), since pyrite is the most abundant mineral in the tailings (around 55%). The highest concentration of Zn was also found in PJMA8 (1,000 m), probably due to the high solubility of zinc sulfide, whereas in all the other

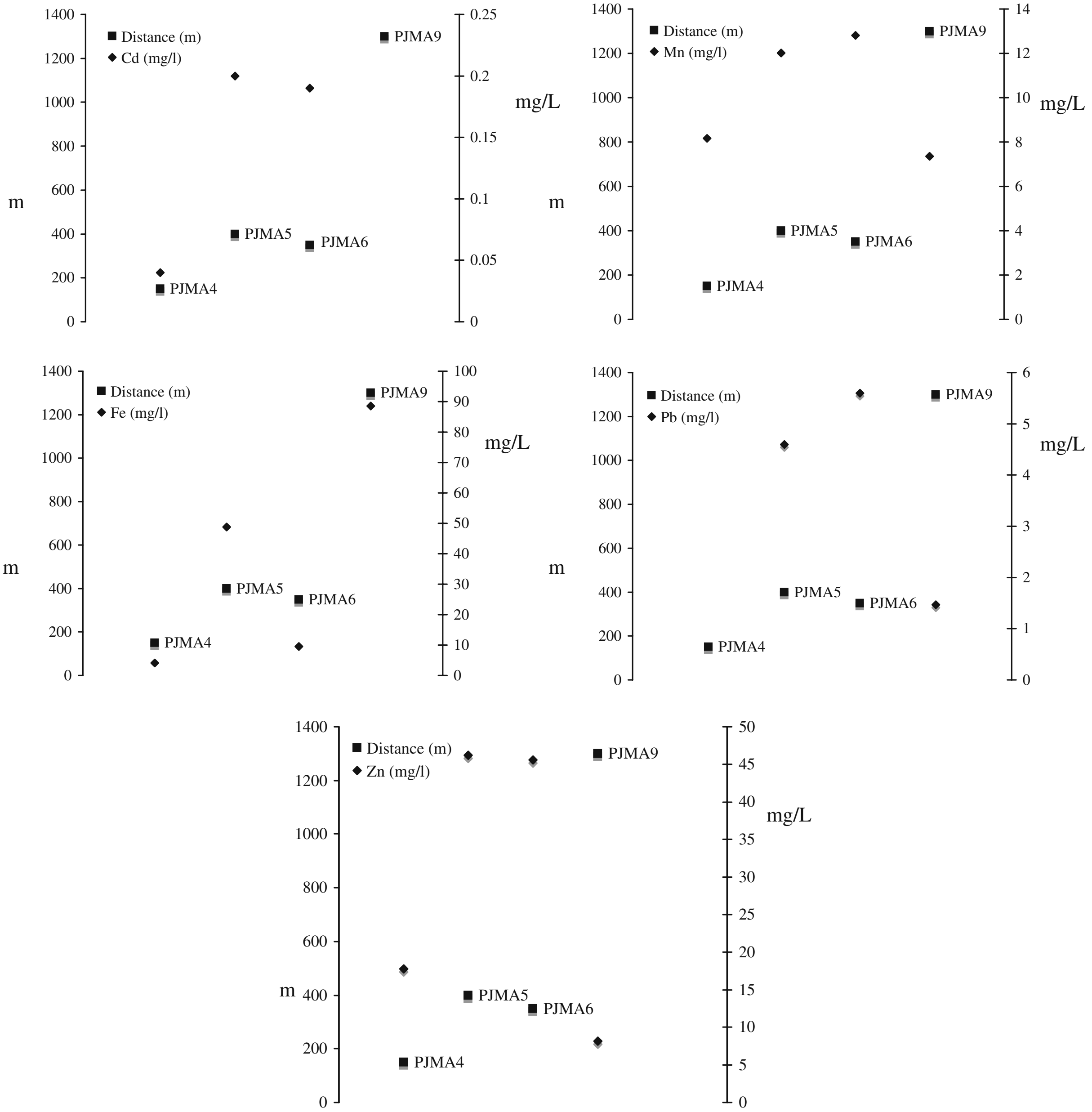

Fig. 5 **a** Relation among sampling points distances to tailings pile and the metals concentration in inner zone. **b** Relation among sampling points distances to tailings pile and the metals concentration in outer zone

sampling points it was very low. The presence of these elements in high concentrations in PJMA8 could be explained by the fact that this water is extracted from underground mining activities and then deposited in superficial pools; where the water is exposed to atmospheric conditions, accelerating oxidation processes and liberation of metals are typical of AMD.

Chemical speciation

The distribution of the different mineral species in solid phase, as well as the secondary minerals which are precipitated, in equilibrium or dissolved, and the ionic strength of the water samples, are shown in Table 4. The characteristic metals from AMD problems, which are present

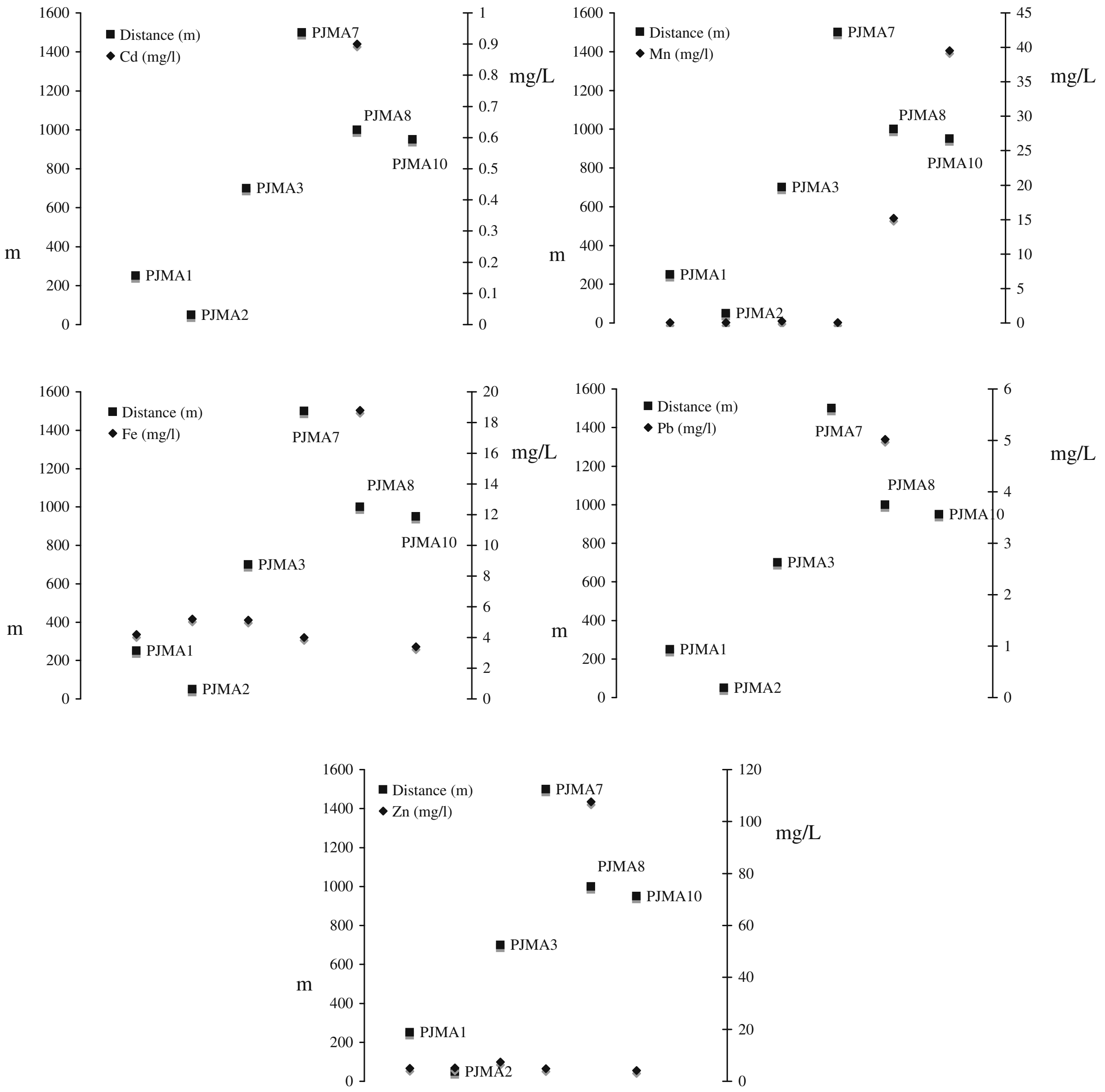

Fig. 5 (continued)

in the superficial waters sampled, are discussed below:

Manganese

The major species of manganese in superficial waters in the study area could include hausmannite [$Mn^{++}Mn^{+++}2O_4$], manganite [MnO (OH)], pyrochroite [$Mn(OH)_2$], and pyrolusite (MnO_2). The mean abundance is in the order: manganite > pyrochroite > pyrolusite > hausmannite. All these species are mobile in water (Reimann and Caritat 1998). For this reason, Mn is dissolved in superficial water, and might be due to natural weathering of rocks. The low concentrations indicate that this metal does not pose a contamination problem in the area.

Table 4 Chemical speciation of most representative water samples, saturation indexes (SI)

Mineral phase	Inner zone	Outer zone				
	PJMA4[b]	PJMA1[b]	PJMA2[a]	PJMA2[b]	PJMA2[c]	PJMA7[b]
Ionic strength	8.046^{-2}	1.411^{-3}	6.303^{-4}	7.753^{-4}	2.906^{-4}	1.585^{-3}
Anhydrite, $CaSO_4$	−0.21					
Celestite, $SrSO_4$	−0.46					
Calcedony	0.36	−0.52	−0.41	−0.5		0.18
Crisotile, $Mg_3Si_2O_5(OH)_4$	−5.03	−5.51	−4.28	−19.97		−5.86
$Fe(OH)_{3(a)}$		2.94	2.8	−3.39	3.35	
FeS $_{(ppt)}$					−83.48	
Goethite, FeO(OH)		8.83	8.7	2.51	9.24	
Gypsum, $CaSO_4{\cdot}2(H_2O)$	0.02					
$H_2S_{(g)}$	−59.8				−87.37	
Hausmannite, $Mn^{++}Mn^{+++}2O_4$	−12.7	−9.84	−8.18	−28.82		−14.16
Hematite, Fe_2O_3		19.63	19.81	7.32	20.28	
Mackinawite, $(Fe,Ni)S_{0.9}$					−82.74	
Manganite, MnO(OH)	−5.42	−4.32	−4.25	−11.86		−6.11
Melanterite, $Fe(SO_4){\cdot}7(H_2O)$					−12.42	
Pyrite, FeS_2					−137.51	
Pyrochroite, $Mn(OH)_2$	−6.06	−5.89	−5.87	−10.91		−7.16
Pyrolusite, MnO_2	−11.1	−8.75	−7.66	−18.08		−10.72
Quartz, $SiO_2(a)$	0.77	−0.12	−0.03	−0.11		0.52
Sepiolite, $Mg_4Si_6O_{15}(OH)_2{\cdot}6(H_2O)$	−2.87	−4.73	−3.95	−14.5		−3.87
$SiO_{2(a)}$	−0.49	−1.36	−1.23	−1.32		−0.65
Sphalerite, (Zn,Fe)S	−47.05				−70.96	
Willemite, Zn_2SiO_4	−0.62		0.71			−1.37
$Zn(OH)_2$	−2.43		−1.75		1.24	−2.91

Wateq4f was the database used, and is included in the hydrogeochemical modeling program PHREEQC (Parkhurst and Appelo 1999)

Blank spaces indicate mineral could not be quantified

[a] April 2005 (sampling date)

[b] September 2005 (sampling date)

[c] January 2006 (sampling date)

Iron

The mean abundance of iron species is in the order $Fe_2O_3 > FeO(OH) > Fe(OH)_3 > Fe(SO_4){\cdot}7(H_2O) > (Fe,Ni)S_{0.9} > FeS > FeS_2$. In the outer zone, water is saturated with respect to hematite (Fe_2O_3), goethite [FeO(OH)], and iron hydroxide [$Fe(OH)_3$]. Under low pH conditions, the species melanterite [$Fe(SO_4){\cdot}7(H_2O)$], mackinawite [$(Fe,Ni)S_{0.9}$], FeS, and pyrite (FeS_2) are mobile, specially in the inner zone. Fe concentrations are the highest in almost all the superficial water bodies analyzed. According to Reimann and Caritat (1998), Fe is toxic to humans in drinking water at levels >200 mg/L, but environmental norms indicate that PML for human consumption is 0.3 mg/L.

Zinc

The mean abundance of its speciation is in the order sphalerite (Zn,Fe)S > willemite (Zn_2SiO_4). Sphalerite seems to be the principal mineral liberating Zn. Zinc was the predominant dissolved metal in both inner and outer zones, and will pose contamination risk mainly to the superficial water in the study area.

Ionic strength (I)

The ionic strength (I) ranges between 9.303^{-4} and 8.057^{-2}. According to Alpers and Blowes (1994) and Appelo and Postma (1999), the ionic strength for freshwater is normally less than 0.02, while seawater has ionic strength of about 0.7. Also

Deutsch (1997) reported that ionic strength of most ground waters is in the range of 10^{-2} to 10^{-3}. The values of the ionic strength show that superficial water samples from the area are fresh. Hence, the results of I indicate greater solubility and hence mobility of the dissolved species such as Zn and Fe in the study area (especially in inner zone).

Tailings mineralogy

Lizárraga-Mendiola et al. (2008) reported that the mineral average composition of tailings, in decreasing order is pyrite (55%), quartz (15%), chlorite (10%), muscovite (6%), cristobalite (5%), epidote (5%), gypsum (2%), and sphalerite (2%). Vega et al. (2004) indicated that the extraction of metal ores causes generally a multi-elemental contamination (Mn, Fe, Cd, and SO_4^{2-}) of the environment, especially superficial and/or sub superficial runoffs located near the tailings pile. In the study area a multi-elemental contamination might be due to acid leachates generated from tailings (AMD).

The results of the EDS-X ray microanalysis in Table 5, and Fig. 2a–g present the following: It is observed that the predominant elements in order of concentration are S > Fe > Si > Al > Na > Zn > Mg > Ca > As > Cu > K > Pb > Mn > Au > Ag. These results present variations in their concentrations. This is due to the following factors: (1) some samples were taken close to the saturated area of the pile (northern part of the tailings pile), whereas others were taken in the driest area (major exhibition to weathering conditions), (2) the samplings were taken in different times of the year (dry and rainy seasons), favoring also a major and minor exhibition of tailings to the natural weathering conditions, respectively (for location, see Fig. 1b and Table 3).

From the microanalysis results, the following can be mentioned: (a) in the sample PJJ01-0404, it is observed that S and Fe (13 and 11%, respectively) are among the principal elements. Nevertheless, the peaks of (Zn 3%) and (Pb 1%) in the diffractogram also indicate the presence of minerals of sphalerite and galena, respectively. The mineral particles have a predominant cubic morphology type, with thicker particles (pyrite),

Table 5 Tailings mineralogy obtained through EDS semi-quantitative microanalysis, using the scanning microscope WDS/EDS system

Element	PJJ01[a]	PJJ02[a]	PJMC[a]	PJJ01[b] (%)	PJJ05[b]	PJJ06[b]	PJJ02[c]	Average
S	13.35	21.68	22.49	13.40	14.41	20.80	35.19	20.18
Si	12.97	5.08	4.52	8.90	10.14	5.72	11.80	8.44
Al	7.67	2.47	2.31	7.47	6.88	1.66	6.02	4.92
Zn	3.06	2.04	1.99	1.93	2.71	2.55	2.06	2.33
Cu	0.55	1.07	0.57	0.72	0.57	0.91	0.67	0.72
Pb	0.99		1.31	1.33	0.00	0.00		0.51
As	0.00	0.65		0.81	0.52	0.72	1.71	0.73
Au	0.00	0.61	0.00	0.00		0.00		0.08
Ag	0.00	0.00			0.00	0.00		0
Fe	10.74	22.06	20.14	12.95	13.87	22.23	34.47	19.49
Mn	0.16		0.09				0.18	0.14
Ca	0.61	0.76	0.55	1.31	0.78	0.64	2.48	1.01
K	1.16	0.56	0.39	0.55	0.29	0.37	1.56	0.69
Na	4.52	0.42	2.20	5.46	5.92	1.72	1.71	3.13
Mg	1.49	0.93	0.95	4.26	3.94	1.00	1.17	1.96
O	42.74	40.83	42.29	40.84	39.64	41.69		35.43

Blank spaces indicate that concentrations were lower than the detection limit of the equipment

[a] April 2004 (sampling date)

[b] April 2005 (sampling date)

[c] August 2005 (sampling date)

and particles of minor size (possibly galena), (b) in the sample PJJ02-0404, the predominant elements are S (22%), Fe (22%), Al (2%), and Zn (2%); in this sample, the presence of Pb was not detected, although it is not discarded that it also contains galena and in minor quantities some aluminosilicates, it is possible that their concentrations are minimal. Zn is in lower percentage, therefore, possibly in this sample sphalerite is present, (c) the sample PJMC-0404 is a composite of different points of the tailings pile (PJJ01, PJJ02, and PJJ03). Their chemical composition is more homogeneous, predominating S (22%), Fe (20%), Al (2%), Zn (2%), and Pb (1%); this is the only sample where As could not be quantified, (d) the sample PJJ01–0405 in contrast to the previous ones, presents three predominant minerals in tailings: pyrite > sphalerite > galena. The latter mineral exists as incrustation in the contour of sphalerite particles, (e) in sample PJJ05–0405, particles of pyrite have a laminated form, in contrast with the previous samples where particles have a predominant cubic morphology. A large quantity of galena particles was also observed, (f) in sample PJJ06-0405 the cubic shape of pyrite particles is easily observed. As in the other samples, the particles of galena are much smaller than the particles of pyrite. On the other hand, the sphalerite particles size are larger than in the other samples; and (g) sample PJJ02–0805 is the only one where the mineral particles of sphalerite are almost as large as those of pyrite; the elemental content of this microanalysis is: S (35%), Fe (34%), Al (6%), and Zn (2%). In accordance with the EDS-X ray analysis presented in this article, the most abundant sulfide minerals contained in these tailings are pyrite and sphalerite; this explains the prevalence of Fe and Zn, as well as SO_4^{2-} in the superficial runoff (product of the AMD migration).

Mineral liberation

In the original mineral (before being processed), it is observed that galena and sphalerite reached a liberation >80% up to sizes of 8 μm (Fig. 3a). In the case of galena, this low liberation is caused by the high association grade that it presents with sphalerite particles. Free chalcopyrite particles represent more than 35% at sizes less than 70 μm. In the case of pyrite and gangue (the commercially valueless material in which ore is found during processing), the liberation grade is higher than 70 and 95%, respectively, at any particle size. In the tailings sample, it can be observed that pyrite has a liberation of 95% at any particle size (from 8 to 80 μm; Fig. 3b). The rest of the minerals, galena, sphalerite, and chalcopyrite, tend to reduce the liberation at diameters larger than 8 to 80 micrometers in 18, 30 and 42%, respectively.

The degree to which individual grains are exposed, depends to a great extent upon the size of the individual grains relative to the size of the rock sample in which they are contained. Atmospheric pyrite oxidation requires that part of the mineral grain is exposed or liberated by leaching, and so, the smaller the grain size, the larger the surface area exposed will be. As it observed in the microscope, the particle tends to be liberated when exposed to rainwater and oxygen diffusion due to the structure of the mineral grains (Fig. 3c). It has been documented that in the upper part of tailings piles (non saturated zone) highly complex geochemical processes take place (dissolution, precipitation of secondary-tertiary phases, redox reactions, adsorption, etc.), due to the interaction between the fine grains of sulfide minerals (Alpers and Blowes 1994).

Conclusions

In the mining area studied, the release of zinc and lead mainly, is due to the presence of sphalerite and galena in the tailings, which become more reactive in the presence of pyrite, specially the galena. The extension of the natural removal of zinc, lead, copper and other metals can reach, depends, among other factors, on the pH in solution, the presence or absence of minerals that favor the neutralization of the oxidized minerals, as well as the tailings mineralogy, which in this case lack carbonates. The mineral grain size showed that smaller particle size could liberate more ions to the environment; in this specific research, where pyrite and sphalerite are the most abundant sulfide minerals, these could be the main factors that contribute to accelerate the AMD process in tailings that are in contact with atmospheric oxygen and rainwater. On the other hand, maximum ions concentrations (mg/L) measured in superficial waters found were, in the outer zone: As, Cd, Fe, Mn, Pb, SO_4^{2-}, and Zn, and in the inner zone are As, Cd, Fe, Mn, Pb, SO_4^{2-}, and Zn. The presence of these ions that exceed the permissible maximum limits for human consume, could be associated to tailings mineralogy and acid leachates generated in tailings pile.

While the metals are transported far from its origin place (in this case, the tailings pile that causes the AMD), its concentration in the superficial runoff must be controlled and groundwater must be monitored. As preventive measurements to reduce the oxidation of tailings at the closure of this pile it is suggested: (a) to develop monthly plans of sampling and analyses which include the cartography of the tailings pile at different depths and greater density. This can facilitate the proposal of other alternatives that might help to diminish the impact that this tailings pile causes in the zone, and (b) to design and place an impermeable covering on the surface of the pile, which helps to avoid the oxygen and rainwater diffusion through the tailings.

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