Acid mine drainage from the Panasqueira mine and its influence on Zêzere river (Central Portugal)

Carla Candeias [a,*], Paula Freire Ávila [b], Eduardo Ferreira da Silva [a], Adelaide Ferreira [b], Ana Rita Salgueiro [a], João Paulo Teixeira [c]

[a] University of Aveiro, Geosciences Department, GeoBioTec – Geobiosciences, Geotechnologies and Geoengineering Research Center, Campus de Santiago, 3810-193 Aveiro, Portugal
[b] LNEG-National Laboratory of Energy and Geology, 4465-956 S. Mamede Infesta, Portugal
[c] National Institute of Health, Environmental Health Department, Rua Alexandre Herculano, 321, 4000-055 Porto, Portugal

ABSTRACT

The Panasqueira hydrothermal mineralization, located in central Portugal, is the biggest Sn–W deposit of the Western Europe. The main evidences of the mining exploitation and ore treatment operations are testified with huge tailings, mainly, in the Rio and Barroca Grande areas. The mining and benefication processes, at the site, produces metal rich mine wastes. Oxidation of sulfides tailings and flow from open impoundments are responsible for the mobilization and migration of metals from the mine wastes into the environment. Acid mine drainage (AMD) discharged from Rio tailing has a pH around 3 and high metal concentrations. In Zêzere river, Fe and As are the most rapidly depleted downstream from AMD once As adsorbs, coprecipitate and form compounds with iron oxyhydroxides. The Zêzere river waters are oversaturated with respect to kaolinite and goethite and ferrihydrite can precipitate on stream with a near-neutral pH. At sites having low pH the dissolved Fe species in the water, mainly, occur as sulfate complexes due to a high SO_4 concentration. Melanterite ($Fe^{2+}(SO_4)\cdot 7(H_2O)$) and minor amounts of rozenite ($Fe^{2+}(SO_4)\cdot 4(H_2O)$) and szomolnokite ($Fe^{2+}(SO_4)\cdot(H_2O)$) were observed on Rio tailing basement.

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1. Introduction

Acid mine drainage (AMD) is a well-known international environmental problem related with both working and abandoned mining operations. Large masses of sulfide minerals are exposed during the mining and milling processes. The generation and discharge of AMD with low pH and containing high concentrations of dissolved metals may seriously disturb the water quality. The key to understand mining effects depends directly on understanding the processes that produce AMD. Acidic drainage is caused by the oxidation of sulfide minerals exposed to atmospheric oxygen. Although acid drainage is commonly associated with the extraction and processing of sulfide-bearing metalliferous ore deposits and sulfide-rich coal, AMD can occur wherever sulfide minerals are exposed to atmospheric oxygen (Blowes et al., 2003). The oxidation of pyrite is a complex hydrobiogeochemical process that adversely affects the water quality of receiving streams by producing acid waters with high metal concentrations. Sulfide ore extraction and processing enhances the rate of pyrite oxidation, increases the rate of acid production, and can cause severe environmental

damage (Plumlee and Logsdon, 1999; Jambor et al., 2003; Nordstrom et al., 2007).

The Panasqueira mine was chosen to be studied due to several factors: (a) it is an active mine; (b) the existence of huge volumes of tailing piles and mud dams, (c) small villages near the mine site; (d) the Zêzere river crosses the area, which supply the Castelo de Bode dam (located 90 km downstream), the main water provider for Lisbon; and (e) the local population strongly depends on the use of land and water for their subsistence. The effect of Panasqueira mining activities and the metals release from acid mine waters to water courses is dynamic and actual (e-EcoRisk, 2007; Ávila et al., 2008; Ferreira da Silva et al., 2013; Candeias et al., 2013; Coelho et al., 2013). Regarding the study presented by Ávila et al. (2008) and its conclusions, mainly related to the dynamics of leaching, transport, and accumulation of some selected metals and metalloids in different media (stream sediments, alluvium, surface waters, impoundment materials, iron coatings, arsenopyrite stockpile material, and ferruginous crust) this study aims to characterize the heavy metal contamination at Zêzere river taking into consideration the physico-chemical properties of the waters sampled on the Zêzere river and along the mine drainage. The main goal of this geochemical research is (a) to characterize the surface water chemical changes that occur along the flow path of Zêzere

* Corresponding author. Tel.: +351 938 065 777; fax: +351 234370605.
  E-mail address: candeias@ua.pt (C. Candeias).

river and (b) predict the minerals which can be precipitated according to the local conditions.

2. Site description

The Panasqueira hydrothermal mineralization is the biggest Sn–W deposit of Western Europe and has been in operation since 1896 to the present date (Smith, 2006; Ferreira da Silva et al., 2013). The mining concession is located geographically in Central Portugal (Fig. 1), between Gardunha and S. Pedro de Açor mountains, at approximately 20 km SW of Serra da Estrela, the highest mountain of mainland Portugal (1993 m). The local topography ranges in altitude from 350 to 1080 m (Reis, 1971), with deep valleys. Climate, which can be an important instability factor, is aggressive with hot and dry conditions during the summer and very cold, rainy, and windy conditions in the winter (Ávila et al., 2008). The mean annual temperature is 12 °C, ranging from 0 °C during the winter to 30 °C in the summer (source www.inag.pt). The streams, with the exception of Zêzere river, are generally dry in the summer and flooded in the winter. The small villages around the mine have a historical dependence on soil and water use – drinking water, agriculture, cattle breeding, fishing and sylviculture.

2.1. Geology and mineralization

According to the paleogeographic and tectonic zoning established by Lotze (1945) and Julivert et al. (1974), this deposit is included in the Central Iberian Zone (CIZ), where the Sn–W deposits, such as Panasqueira, are spatially related to the contacts between the sintectonic muscovite–biotite and the metasedimentary country rocks. A detailed description of the local geology was presented in Ávila et al. (2008). The Panasqueira deposit contains mainly, wolframite, arsenopyrite, chalcopyrite and cassiterite. The Panasqueira deposit consists on a sequence known as the upper Precambrian–Cambrian aged Beira-Schist Formation sequence that consists on a series of stacked, subhorizontal and hydrothermal quartz veins intruding into the Beira schists. No granite crops out in the district, but a granite cupola strongly greisenized with increasingly alteration was penetrated at shallow depths in the mine (Kelly and Rye, 1979). Thermal metamorphism spatially associated with the Hercynian batholith produced a regionally extensive aureole of spotted shales in the schist–graywacke complex. The paragenesis is complex and 4 stages of mineral formation are accepted by most of the authors who have studied this deposit: 1st stage, the oxide silicate phase (quartz, wolframite; cassiterite); 2nd phase, the main sulfide phase (pyrite, arsenopyrite, pyrrhotite, sphalerite, chalcopyrite); 3rd stage, the pyrrhotite alteration phase (marcasite, siderite, galena, Pb–Bi–Ag sulfosalts); and 4th stage, the late carbonate phase (dolomite, calcite) (Noronha et al., 1992; Correa and Naique, 1998; Corrêa de Sá et al., 1999; Breiter, 2001). At Panasqueira, more than 65 minerals including sulfides, sulfosalts, oxides, carbonates, silicates, phosphates, and tungstate minerals, have been identified (Kelly and Rye, 1979).

2.2. Mining activity

The Panasqueira mining concession has been in production for over 100 years and is one of the largest economic vein deposits in the world. The first prospecting license was granted in 1895 and the first reference to wolframite mineralization in Panasqueira mine reportedly dated to 1896. The mine produce wolframite and cassiterite concentrates, with secondary production of copper concentrates. Arsenopyrite (the main sulfide) is discarded to the tailings which contain about 30% of As. During the period 1947–2001, the mine produced about 96,456 t of WO_3, 4901 t of SnO_2 and 28,924 t of Cu from more than 27 Mt of rock (Cavey and Gunning, 2006). The long history of mining and milling activities are stated by the presence of huge tailings and mud
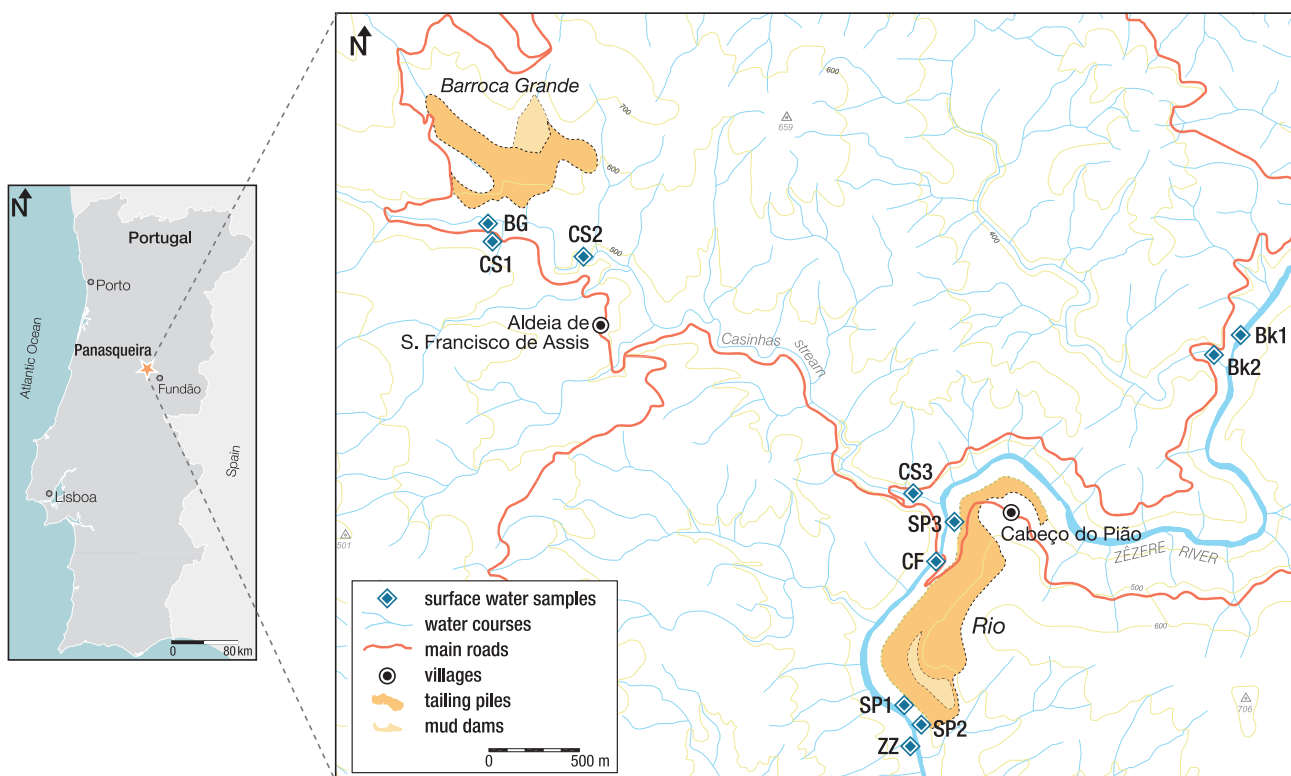

Fig. 1. Location of the Panasqueira mine and the surface waters sampling sites.

dams. Nowadays offices, underground exploration, milling processes, tailing ($\approx$7,000,000 m^3) and mud dams ($\approx$1,193,885 m^3 – one active and one deactivated) are located in Barroca Grande. Until 1996 the underground operations took place in Barroca Grande and the ore were transported by an aerial rope tramway trough 5.1 km to the concentration plant located in Rio. The milling facilities at Rio, located near Zêzere river (Fig. 1), had the advantage of local ore deposits and water from the river for milling operations (Crosby, 2001). The Rio site consists in a large area of tailings, a seepage collection and treatment system. With a long history of mining and milling at Rio, a significant volume of tailings materials was generated ($\approx$1,200,000 m^3) with an elevation of approximately 350 m, slopes of about 35° and three main types of materials: coarse grained waste rock composed primarily of schist and quartz; fine grained mill tailings originating from mill operations composed by sand, mud, and slush and an pile with arsenopyrite (9400 m^3) separated during mill flotation processing, that remained exposed until June 2006 when was capped with geotextile and layers of clay (Gilchrist and Mahmoud, 1999; Crosby, 2001; e-EcoRisk, 2007). The muds and slush were discharged into a pond that was intentionally created for that purpose. The pond is an open air impoundment and contains 731,034 m^3 of rejected ore concentrates with high metal levels (Ávila et al., 2008). The piles and open air impoundments are exposed to the atmospheric conditions for a long time, which affect their chemical, mineralogical, physical and geotechnical elements. Infiltration of rain water occurs across the tailing area, this water carries the acid products of sulfides oxidation. To prevent acid drainage, two water treatment plants exist in Panasqueira mine, one in Barroca Grande and other in Rio, where the acid waters formed are collected, pumped and treated. Acid effluents are neutralized with lime

Ca(OH)$_2$ which promotes metal precipitation and flocculation when pH increases. After this treatment clean water is conducted to the ore dressing plant, or discharged directly in the Zêzere river, while precipitates are disposed via pipeline in the mud dam (Gilchrist and Mahmoud, 1999). On the bottom of Rio tailing a channel system has been installed to collect the seepage, of acid mine drainage water (AMD), nevertheless during the winter and periods of heavy rainfall the system easily overload resulting in mixing of AMD directly with the Zêzere river.

3. Materials and methods

3.1. Field sampling

The surface waters sampling sites (Fig. 1) were chosen to evaluate the influence of the tailings and AMD on the nearest streams and to know the way of the contamination diffusion in the Zêzere river. They include three samples in Casinhas stream downstream Barroca Grande tailing (CS1, CS2 and CS3) and one sample from the mine adit at Barroca Grande (BG). In Rio site, the sampling, include three AMD seepage waters (SP1, SP2 and SP3) and in the main river include two local background waters (Bk1 and Bk2), one sample after Casinhas stream confluence with Zêzere river (CF) and one sample from Zêzere (ZZ) but downstream of both tailings areas (Barroca Grande and Rio).

Samples were collected and filtered from each site using a clean 1 L acid-washed polyethylene bottle and stored at 4 °C until analyzed. Samples for metal analysis were preserved, with pH reduction to 2.0 using HNO$_3$, avoiding Fe hydroxide precipitation. Temperature, pH, and specific conductivity of the surface waters were recorded at each site.

Table 1
Physicochemical data of seepage waters, surface waters from Casinhas stream and Zêzere river.

Var	Units	Seepage waters				Casinhas stream			Zêzere river			
		SP1	SP2	SP3	BG	CS1	CS2	CS3	Bk1	Bk2	CF	ZZ
pH	–	3.0	2.9	3.2	3.9	4.3	5.7	5.7	6.8	7.1	6.9	6.8
SC	mS cm^{-1}	3.63	4.40	2.02	1.26	0.35	1.09	0.85	0.059	0.037	0.070	0.076
SiO$_2$	mg L^{-1}	103	108	99	30	18	16	16	10	12	10	11
Cl	mg L^{-1}	5	6	4	5	5	7	6	5	4	5	7
SO$_4$	mg L^{-1}	2990	3720	1400	727	152	605	441	4	4	9	12
F	mg L^{-1}	nd	nd	nd	nd	nd	nd	nd	0.11	0.035	0.11	0.18
HCO$_3$	mg L^{-1}	nd	nd	nd	nd	nd	nd	nd	15.3	9.8	14	13.4
PO$_4$	μg L^{-1}	nd	nd	nd	nd	nd	nd	nd	65	65	65	65
NO$_3$	mg L^{-1}	nd	nd	nd	nd	nd	nd	nd	4	1.2	3.9	3.7
NO$_2$	μg L^{-1}	nd	nd	nd	nd	nd	nd	nd	130	5	70	60
Na	mg L^{-1}	17.8	19.3	11.8	12.7	5	12	10.4	6	4	7	7
K	mg L^{-1}	6	0.1	1	2	1	5	4	1	0.3	1	1
Mg	mg L^{-1}	274	357	103	95	23	73	56	1	1	2	3
Ca	mg L^{-1}	287	401	175	107	22	120	87	3	1	3	4
Al	μg L^{-1}	149,000	161,000	99,000	6100	1500	800	600	13	7	134	266
As	μg L^{-1}	2140	544	146	48	5[a]	13[a]	13[a]	2	4	3	4
Cd	μg L^{-1}	464	393	226	88	15	58	40	0.2	0.2	0.9	1.6
Cu	μg L^{-1}	42,700	54,300	20,100	2100	190	600	510	6.3	3	42.9	121
Fe	μg L^{-1}	82,500	91,000	9400	1700	100	100	290	40	<30	<30	130
Mn	μg L^{-1}	88,700	92,600	22,300	10,200	1100	7000	4100	19	4	85	256
Zn	μg L^{-1}	49,200	44,500	21,900	12,400	2000	6300	4800	18	21	105	181
Li	μg L^{-1}	1170	1010	751	192	32	140	101	<4	<4	<4	4
Be	μg L^{-1}	57	61	38	<10	<10	<10	<10	<0.2	<0.2	<0.2	<0.2
Co	μg L^{-1}	2620	3330	1140	125	6	84	60	0.3	0.2	3.1	9.6
Ni	μg L^{-1}	2150	2830	1140	397	110	273	200	<1	1	4	9
Sr	μg L^{-1}	658	507	380	396	75	338	256	18.3	9	19.9	21.2
Pb	μg L^{-1}	<22	<22	<22	<22	<22	<22	<22	<0.3	<0.3	<0.3	<0.3
Y	μg L^{-1}	428	542	322	33	6	19	19	0.2	<0.1	0.7	1.3
TDS	mg L^{-1}	2360	2860	1313	819	228	707	553	38.4	24.1	45.5	49.4

[a] These three values are lower than the quantification limit of the ICP-MS method but higher than the detection limit of the samples. Samples SP1, SP2 and SP3 – seepage waters collected in Rio tailing; sample BG – mine entrance in Barroca Grande; samples CS1, CS2 and CS3 – Casinhas Stream downstream Barroca Grande tailing; samples Bk1 and Bk2 – Zêzere river upstream Rio tailing; samples CF and ZZ – Zêzere river; nd – not determined.
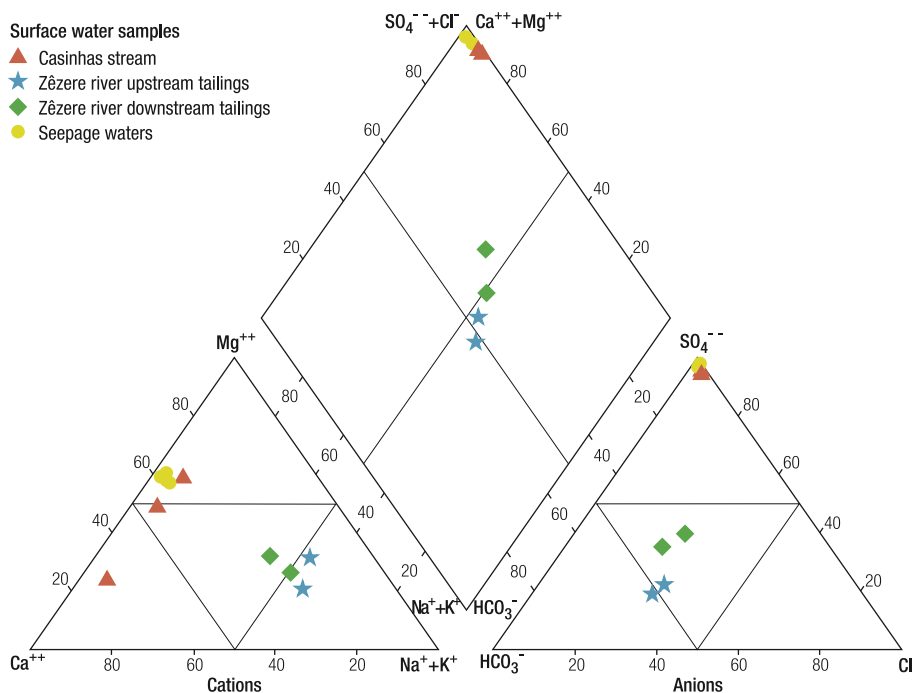
Fig. 2. Piper's diagram showing the plot of chemical data of Casinhas stream, Zêzere river and seepage waters samples.

3.2. Chemical analysis

Surface water samples were analyzed without pre-concentration. The analyzed elements include major anions (HCO_3^-, Cl^-, NO_3^-, and SO_4^{2-}), major cations (Na, K, Mg^{2+} and Ca^{2+}), as well a suite of dissolved trace metals (Ag, Al, As, Bi, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb, S, Sb, and Zn). Unacidified samples were analyzed using a Dionex 1000i ion chromatography (IC) Work33 station to determine the Cl^-, NO_3^-, and SO_4^{2-} concentrations. Anisocratic elution with a sodium bicarbonate–sodium carbonate eluent was employed together with a Dionex AS4-SC column. The alkalinity was determined in situ by volumetric titration on filtered unacidified samples using H_2SO_4 acid 0.16 N.

Although standards were prepared containing only the above anions, other anions would have been detected if present at levels greater than ≈0.1 mg L^{-1}. For concentrated samples, dilution was required for reliable anion analysis. The concentrations of major cations and trace elements in acidified waters were determined using mass inductive plasma spectrometry (ICP-MS) at the LNEG accredited lab. Reagent blanks and duplicate samples were inserted into each batch for quality control (Ramsey et al., 1987). The geostandards AQUACHECK and EAA 4 were used to check the validity and reproducibility of the results. Typical uncertainties, including all error sources, are ≈6% for the trace elements, and between 2% and 7% for the major anions, depending on the concentration levels. The limit of detection for the analyzed trace metals ranges between 0.05 and 10 mg L^{-1}.

3.3. Mineralogical studies

The mineralogical characterization of samples was performed by X-ray diffraction (XRD) using a Philips diffractometer (model X'Pert). Working conditions were automatic divergence slit, Cu Kα monochromatic radiation, graphite monochromator, 20 mA and 40 kV. Samples were run at a speed of 0.05° 2θ/min (2–70°).

The mineral constituents (including efflorescence) were identified by X-ray diffraction at LNEG.

3.4. Data analysis

Piper diagram (PD): widely used to study the similarities and differences in the composition of waters and to classify them into certain chemical types (Chadha, 1999). As described by Karanth (1987) the PD show the essential chemical character of different constituents in percentage reacting values, expressed in milligrams equivalent, for each water type. Some more detailed information of these plots might be seen in Freeze and Cherry, 1979.

Ficklin diagram: in order to interpret variations in drainage water chemistry Plumlee et al. (1992) developed one diagram, based on pH and the sum of the base metals Zn, Cu, Pb, Cd, Co and Ni. These parameters were selected rather than more common metals such as Fe, Al and Mn because have proven to be the most diagnostic in differentiating between different geologic controls (INAP, 2009).

PHREEQC code and WATEQ4F: is a geochemical modeling software based on ion-association aqueous model and is capable of describing chemical reactions and transport processes in waters. It is based on equilibrium chemistry of aqueous solutions with minerals, gases, solid solutions, exchangers, and sorption surfaces. PHREEQC can be used, among others, as a speciation program to calculate saturation indices (SI) and the distribution of aqueous species (Parkhurst and Appelo, 1999). Additionally WATEQ4F is also a chemical speciation code for waters. It uses the water field parameters of temperature, pH, Eh, dissolved oxygen and alkalinity, and also the chemical analysis computing the distribution of aqueous species, ion activities, and mineral saturation indices that specify the propensy of a water to dissolve or precipitate a set of minerals (Drever, 1988; Nordstrom and Munoz, 1986). The WATEQ4F results are used primarily to examine the tendency of water to reach mineral solubility equilibrium as a constraint on interpreting the chemistry of waters. These results are a helpful
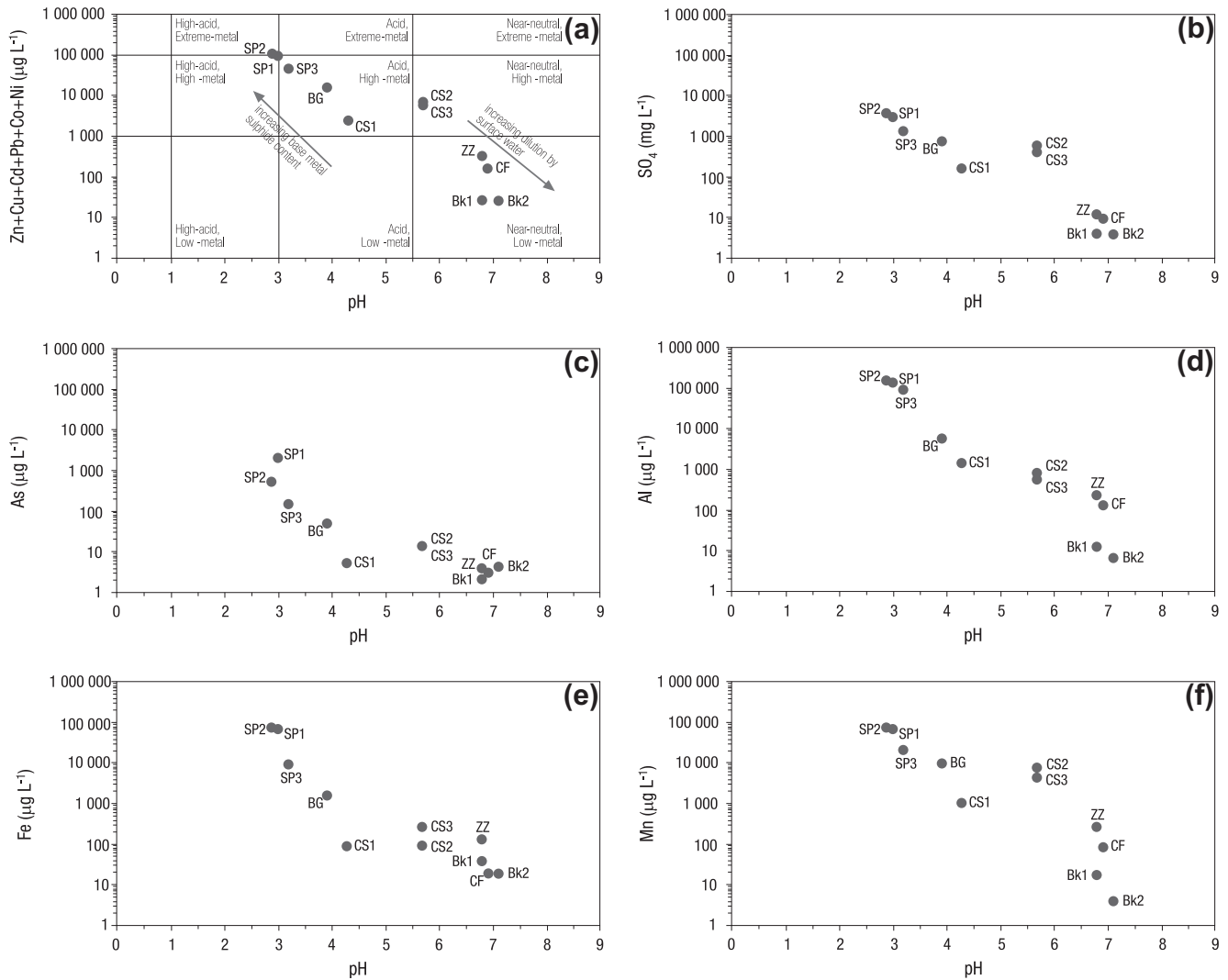
Fig. 3. Ficklin diagram (a) with the sum of dissolved base metals Zn, Cu, Cd, Pb, Co and Ni in water samples. The boundaries and names of metal bins were proposed by Plumlee et al. (1992, 1999) in order to classify different drainage compositions. Diagram showing AMD as a function of sulfate concentrations (b). Plot of mine drainage from Arsenic (c), Aluminum (d), Iron (e) and Manganese (f).

implement used for reaction modeling with the PHREEQC software (Ball and Nordstrom, 1991).

4. Results and discussion

4.1. Water geochemistry

The results presented in Table 1, show that water samples can be divided distinctly into three main groups based on its location and also in the pH and electric conductivity (SC) conditions: the Casinhas stream samples with $4.3 <$ pH < 5.7 and $0.35 <$ SC < 1.09 mS cm^{-1}; the Zêzere river waters with $6.8 <$ pH < 7.1 and $0.037 <$ SC < 0.076 mS cm^{-1} and the seepage water with a $2.9 <$ pH < 3.9 and $1.26 <$ SC < 4.40 mS cm^{-1}. These different types of water represent distinct hydrogeochemical processes. The trace metal concentrations in the seepage water and water collected in the Casinhas stream are higher than the concentration in the Zêzere water. Sulfate concentrations cover a range from 4 to 3717 mg L^{-1} and the highest concentrations are associated with waste piles and correlate with low pH values ($r = -0.98$, $p < 0.05$). The TDS values of the seepage waters ranged from 819 to 2860 mg L^{-1}. The

Casinhas stream waters showed higher values of TDS from 227.5 to 707.2 mg L^{-1} than those of the Zêrere River which ranged from 24.1 to 49.4 mg L^{-1}.

Table 1 Correlation coefficients of data (significance level $p < 0.05$) indicate a strong association of SO_4^{2-}/Ca^{2+} (0.98); SO_4^{2-}/Mg^{2+} (0.99); SO_4^{2-}/Na^+ (0.93); SO_4^{2-}/Al (0.96); SO_4^{2-}/Mn (0.98); SO_4^{2-}/Fe (0.96); SO_4^{2-}/As (0.72); SO_4^{2-}/Cd (0.97); SO_4^{2-}/Cu (0.98) and SO_4^{2-}/Zn (0.98). The high positive correlation with Ca, possibly, reflects the influence of gypsum and calcite dissolution plus sulfide oxidation. Table 1 shows that major ions contents tend to increase with the decrease of pH, whereas (HCO_3^- and Cl^- showed positive correlation with pH, indicating the dissolution of minerals related to the host rock composition. Based on these observed hydrogeochemical characteristics, along with the major mineral constituents in the rock and ores, it is suggested that the seepage waters are related to sulfide weathering and dissolution of secondary minerals whereas the Zêzere river chemical characteristics of the waters are mainly controlled by dissolution of carbonate and silicate minerals.

Hydrochemical compositions of the water samples were plotted in Piper trilinear diagram (Fig. 2). Generally, the seepage and Casinhas stream waters are classified as Mg/Ca – SO$_4$ type waters. The

surface waters collected upstream the Zêzere river are Na-HCO₃ type while the downstream Zêzere waters have been classified as mixed waters between Mg/Ca and CO₃/SO₄ type.

The drainage discharges from Rio tailing are typical mine waters and belong to the Ca/Mg-SO₄ type. The results show that these three groups of water have different geochemical evolutionary paths during their circulation. The decreasing order of the abundance of major ions in seepage and Casinhas stream waters is $SO_4^{2-} > Ca^{2+} > Mg^{2+} > Si > Na^+ > Cl^- > K^+$. The Zêzere river waters have different pattern from the previous ones and amongst themselves, upstream both tailings the water reveal the following order: ($HCO_3^- > Si > Na^+ > Cl^- > SO_4^{2-} > NO_3^- > Ca^{2+} > Mg^{2+} > K^+$) and downstream the effects of mining contamination is notorious once the decreasing order of the abundance of major ions is ($HCO_3^- > SO_4^{2-} > Si > Na^+ > Cl^- > NO_3^- > Ca^{2+} > Mg^{2+} > K^+$). The oxidation of sulfide minerals in mine-waste rock piles and tailings impoundments generates acidic waters containing high concentrations of SO_4^{2-}, Fe (II), and other metals. According to Blowes et al. (2003) a sequence of geochemical reactions occurring in the mine wastes and in underlying aquifers results in profound changes in the concentrations of dissolved constituents and in the mineralogy and physical properties of the mine waste and aquifer materials. The Casinhas stream and seepage waters show low pH and are enriched in sulfate ions but also in some of the major and trace elements.

Low-pH conditions promote the dissolution of many metal-bearing solids and the metals desorption from solid surfaces. The probable source of sulfate and heavy metals are the oxidation of sulfide minerals, mainly arsenopyrite, but also pyrite and chalcopyrite. These acidic waters are displaced into underlying or adjacent geological materials, or it is discharged directly to the adjacent surface water flow system. The geochemical reactions of these waters with the gangue minerals result in progressive increases in pH through acid neutralization reactions and the attenuation of the concentrations of dissolved metals released from mine wastes.

According to the Ficklin diagram (Fig. 3a) the Panasqueira waters can be separated in four groups: (1) high-acid and extreme metal content; (2) acid and high-metal content; (3) near neutral and high metal content; and (4) near neutral pH and low metal content. The first three groups represent the seepage and the Casinhas stream waters, and the fourth group includes the Zêzere river samples, collected upstream and downstream the Rio tailing. According to Plumlee et al. (1999) the group classified as high acid and extreme metal rich are typical of drainage water derived from polymetallic deposits characterized by low buffering potential. The most polluted waters are in or close to the mine tailing, where the metal dispersion and acidity generation is clearer. Two of the Casinhas stream samples also show a high metal content but with a pH values near neutral. On the other hand the waters collected in Zêzere river present a near neutral pH and low contents of metals, more evident on the upstream samples. This high metal contents and low pH reflect the influence of the acidic waters from the tailings and mud impoundments, while the low concentration values and neutral pH reflects the dilution phenomena and the geochemical baselines values of local surface waters. The plots of SO₄, As, Al, Fe and Mn concentrations versus pH values (Fig. 3b–f) show the same trend of increasing metal content with decreasing pH and reflects the greater amounts of sulfide minerals and a smaller content of carbonates and other minerals that consume acid according to Plumlee et al. (1999).

4.2. Water rock interaction

Chemical elements speciation was performed using the PHRE-EQC code in conjunction with the WATEQ4F data base. Fig. 4 shows
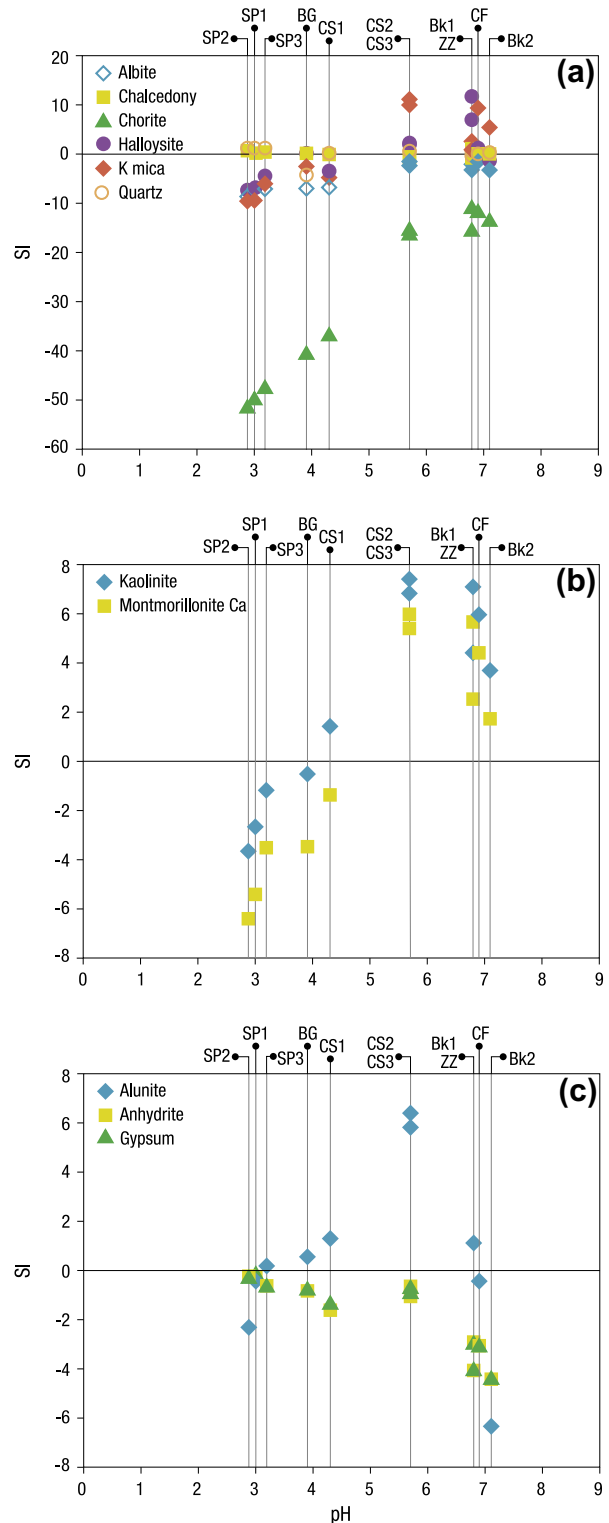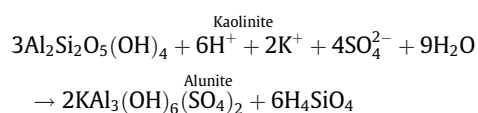

Fig. 4. Saturation indices computed for water samples.

the SI of the waters with concern to various specified minerals. The SI calculation of the representative minerals in waters show that seepage waters with concern to the silicate minerals (Fig. 4a) present a negative saturation index being undersaturated in albite, chlorite, halloysite and K mica or present a positive saturation index and are oversaturated in chalcedony and quartz. The clay

minerals (Fig. 4b), kaolinite and montmorillonite, are undersaturated and most of the sulfates (Fig. 4c), alunite, anhydrite and gypsum, are nearly in equilibrium state in these waters. Regarding Zêzere river waters, according to the calculated SI, they are oversaturated in some of the silicate minerals and clay minerals and undersaturated in sulfates.

The seepage waters (SP1, SP2, SP3 and BG) are mainly saturated or near equilibrium with respect to alunite $KAl_3(SO_4)_2(OH)_6$ while the majority samples of the Casinhas stream and the Zêzere river are oversaturated in gibbsite $Al(OH)_3$. It is thought that an increase in sulfate activity may promote the formation of sulfate minerals (e.g. gypsum, anhydrite and alunite) when the aqueous solution are rich in cations such as Ca, Al and K. The association of alteration minerals alunite + quartz is formed at pH lower than 3.5, while the kaolinite + alunite assemblage develops at pH 4.9 (Perry et al., 1980 and Wirsching et al., 1990). The relationships between alunite and kaolinite were determined by Wirsching et al. (1990) on the basis of experimental studies.

$$\underset{\text{Kaolinite}}{3Al_2Si_2O_5(OH)_4} + 6H^+ + 2K^+ + 4SO_4^{2-} + 9H_2O$$

$$\rightarrow \underset{\text{Alunite}}{2KAl_3(OH)_6(SO_4)_2} + 6H_4SiO_4$$

The alunite is a reaction product of kaolinite with sulfuric acid. According to Inoue (1995), the very low pH values observed in seepage waters, are related to the sulfides oxidation.

The mineralogical composition of samples collected in Rio site (in the dam and in the tailing), reveals the presence of arsenopyrite, scorodite, marcasite, pyrite, mica, quartz, illite, vermiculite, natrojarosite, kaolinite, chlorite, illite, montmorillonite and montmorillonite–vermiculite. The mineralogical composition of Zêzere river stream sediments revealed the presence of mica, quartz, chlorite, kaolinite, feldspar and hematite (XRD identification). At the base of the Rio tailings dam, scorodite ($FeAsO_4 \cdot 2H_2O$), melanterite ($Fe^{2+}(SO_4) \cdot 7(H_2O)$) and minor amounts of rozenite ($Fe^{2+}(SO_4) \cdot 4(H_2O)$) and szomolnokite ($Fe^{2+}(SO_4) \cdot (H_2O)$) were observed and identified by XRD. Acid mine drainage discharged from the Rio tailing (SP1) has a pH of 3.0 and high concentrations of trace metals (Table 1). Also, As concentrations in these samples are high (2140 µg L^{-1} As). Iron concentration in stream waters decreases rapidly downstream with pH rising. Arsenic concentration decreases downstream with the same pattern of Fe (see sample ZZ – Fe = 0.13 mg L^{-1} and As = 4 µg L^{-1}). These results show that Fe and As are the most rapidly depleted elements from AMD and indicates that concentrations of Fe and As decreases by dilution as well as by the formation of precipitate. It is well known that As adsorbs and/or coprecipitates and forms compounds with ferric oxyhydroxide (Dove and Rimstidt, 1985).

5. Conclusions

The present study characterizes the Zêzere river hidrogeochemistry on the basis of physicochemical properties of waters with different locations regarding the tailings: Zêzere river – two samples collected upstream both tailings representing the local background hydrochemistry; two samples collected downstream the tailings; Casinhas stream – three samples downstream Barroca Grande tailing; seepage waters – three samples collected in Rio tailing basement and affected by acid mine drainage and one sample from Barroca Grande mine adit. The seepage and Casinhas stream waters were characterized as ($Ca^{2+} + Mg^{2+}$) SO_4^{2-} water type while the upstream Zêzere river waters are Na-bicarbonate and the downstream Zêzere river waters were classified as being mixed Mg^{2+} and Ca^{2+} bicarbonate/sulfate waters. The acid effluents are neutralized with lime $Ca(OH)_2$ promoting metal precipitation and

flocculation when pH increases. After the treatment clean water is conducted to the ore dressing plant, or discharged directly in the Zêzere river.

By means of the USGS geochemical code PHREEQC, speciation was performed and shows that the seepage waters are undersaturated in most of the silicate minerals and clay minerals and the sulfates are nearly in equilibrium state. The Zêzere river waters are oversaturated in some of the silicate minerals and clay minerals and are undersaturated in sulfates. The majority of the Casinhas stream and the Zêzere river waters are oversaturated in gibbsite. An increase in sulfate activity may promote the formation of sulfate minerals when the aqueous solution is rich in cations such as Ca, Al and K. Acid mine drainage discharged from Rio tailing has pH around 3 and high metal concentration. It was observed that Fe and As are the elements where the concentrations quickly decreases due to adsorption and coprecipitation with ferric oxyhydroxides. Melanterite and minor amounts of rozenite and szomolnokite were observed on Rio tailing basement.

Nevertheless the Zêzere river and the three water reservoir dams located downstream of the Panasqueira mining area: Cabril dam (near Panasqueira mine, is one of the biggest Portuguese dams, high of 136 m, and originates one of the biggest water reserves in the country with capacity of 720,000,000 m^3), Bouçã dam (located between the Cabril dam and the Castelo de Bode dam, has a high of 63 m and a total capacity of 48,400,000 m^3) and Castelo de Bode dam (placed in the limits of Tomar and Abrantes districts, is one of the most important Portuguese dams, presenting a high of 115 m and a total capacity of 1,095,000,000 m^3, and is used for water supply of Lisbon city and neighbor districts) presents, respectively, water with quality compatible with human consume but not for recreation and sportive proposes or fishing support life; the Bouçã dam presents water quality compatible with human consume, recreation and sportive proposes and also with fishing support life and the Castelo de Bode dam presents good water quality for all proposes (e-Ecorisk, 2007). In the near downstream valley area of Panasqueira mine, presently, there are no aquifer systems or areas with hydrological contamination, nevertheless, a catastrophic spill from the Rio tailing and open air impoundment, could be a potential danger and a huge hazard for Zêzere river and the referred water reservoir dams and, obviously, for the entire environment.

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