



VIII Congresso Ibérico
de Geoquímica
XVII Semana
de Geoquímica

AVALIAÇÃO DO IMPACTE DA DRENAGEM DE ÁGUA ÁCIDA NA HIDROGEOQUÍMICA DO RIO ZÊZERE: O CASO DE ESTUDO DA MINA DA PANASQUEIRA, PORTUGAL

ASSESSMENT OF ACID MINE DRAINAGE IMPACT ON HYDROGEOCHEMISTRY OF ZÊZERE RIVER: THE CASE STUDY OF PANASQUEIRA MINE, PORTUGAL

Paula Freire Ávila^{1,2*}, Adelaide Ferreira^{1,2}, Ana Rita Salgueiro², Carla Candeias², Rita Melo³, Eduardo Ferreira da Silva²

¹ Lab S Mamede Infesta LNEG, 4466-956 S Mamede de Infesta, Portugal.paula.avila@lneg.pt

² Universidade de Aveiro, Dept de Geociências, GeoBioTec – Geobiosciences, Technologies and Engineering, Campus de Santiago, 3810-193 Aveiro, Portugal;

³ Universidade de Aveiro, Dept de Geociências, Campus de Santiago, 3810-193 Aveiro, Portugal

Resumo

A mineralização hidrotermal da Panasqueira localiza-se no centro de Portugal e é o maior depósito de Sn-W da Europa Ocidental. A exploração mineira e as operações do tratamento do minério deram origem a escombrelas de grandes dimensões, principalmente, nas áreas do Cabeço do Pião (escombrela do Rio) e Barroca Grande. A exploração e beneficiação dos processos de tratamento no local geraram rejeitados ricos em metais. A oxidação dos sulfuretos existentes na escombrela e o escoamento pela barragem de contenção de lixiviados, são os responsáveis pela mobilização e migração dos metais a partir dos rejeitados da mina até ao meio ambiente. As descargas das drenagens de água ácida da escombrela do Rio possuem um valor baixo de pH ($\text{pH} < 3$) e elevadas concentrações em metais pesados. No Rio Zêzere, o Fe e o As são os elementos que apresentam o mais rápido decaimento de teores uma vez que o As é adsorvido/e ou coprecipita e forma compostos pouco solúveis com os óxidos e hidróxidos de ferro.

Em locais com baixo pH as espécies de Fe dissolvidas ocorrem, principalmente, como sulfatos complexos devido à elevada concentração de SO_4^{2-} . Melanterite ($\text{Fe}^{2+}(\text{SO}_4) \cdot 7(\text{H}_2\text{O})$) e pequenas quantidades de rozenite ($\text{Fe}^{2+}(\text{SO}_4) \cdot 4(\text{H}_2\text{O})$) e szomolnokite ($\text{Fe}^{2+}(\text{SO}_4) \cdot (\text{H}_2\text{O})$) foram observadas na base da escombrela do Rio.

Palavras chave: Drenagem de água ácida, hidrogeoquímica, Mina da Panasqueira, Portugal

Abstract

The Panasqueira hydrothermal mineralization, located in central Portugal, is the biggest Sn-W deposit of the Western Europe. Mining exploitation and ore processing operations left behind huge tailings, mainly in the Cabeço do Pião (Rio tailing) and Barroca Grande areas. The mining and beneficiation processes at the site produced metal rich mine wastes. Oxidation of sulphide 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 discharged from Rio tailings has a pH around 3 and high metal concentrations. In the Zêzere River, Fe and As are the most rapidly depleted downstream from acid mine drainage because arsenic is absorbed and/or coprecipitates and forms compounds with iron oxyhydroxides.

At sites having low pH the dissolved Fe species in the water, mainly, occur as sulphate complexes due to a high SO_4^{2-} concentration. Melanterite ($\text{Fe}^{2+}(\text{SO}_4) \cdot 7(\text{H}_2\text{O})$) and minor amounts of rozenite ($\text{Fe}^{2+}(\text{SO}_4) \cdot 4(\text{H}_2\text{O})$) and szomolnokite ($\text{Fe}^{2+}(\text{SO}_4) \cdot (\text{H}_2\text{O})$) were observed on Rio tailing basement.

Keywords: Acid mine drainage; hydrogeochemistry, Panasqueira mine, Portugal

Introduction

The key to understand mining effects on the surrounding environment depends directly on understanding the processes that produce acid mine drainage (AMD) and high concentrations of soluble constituents in the local hydrogeological setting. Acidic drainage is caused by the oxidation of sulphide minerals exposed to atmospheric oxygen. Although acid drainage is commonly associated with the extraction and processing of sulphide-bearing metalliferous ore deposits and sulphide-rich coal, acidic drainage can occur wherever sulphide minerals are excavated and 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. Sulphide 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 generation of AMD with low pH and containing high concentrations of dissolved metals from mine wastes is an environmental problem of international scale. The Panasqueira mine was chosen for this study because of several factors: (a) it is an active mine; (b) there are huge volumes of tailing piles and mud dams, (c) small villages are near the mine site; (d) the Zêzere River which supplies the Castelo do Bode dam (located 90 km downstream) is the main water supply source for Lisbon and crosses the area; and (e) the local population strongly depends on the use of land and water for their subsistence. 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 characterise 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 to characterise the surface water chemical changes that occur along the flow path of Zêzere River and predict the minerals which can be precipitated according to the local conditions.

Description of the area, geology, mineralization and mining activities

The Panasqueira mine is located in central Portugal, the topography ranges in altitude from 350 to 1080 m (Reis, 1971), with deep valleys. Streams, with the exception of Zêzere River, are generally dry in the summer and flooded in the

winter. 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 study area is located in the Central Iberian Zone (CIZ), where the Sn-W deposits, such as Panasqueira, are spatially related to the contacts between the flysch-type units and the syn-metamorphic muscovite-biotite granites. The Panasqueira deposit contains mainly, wolframite, arsenopyrite, chalcopyrite and cassiterite and lies in a folded metasedimentary 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 spotting 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: 1) the oxide-silicate phase [quartz, wolframite; cassiterite]; 2) the main sulphide phase [pyrite, arsenopyrite, pyrrhotite, sphalerite, chalcopyrite]; 3) the pyrrhotite alteration phase [marcasite, siderite, galena, Pb-Bi-Ag sulphosalts]; and 4) the late carbonate phase [dolomite, calcite] (Breiter, 2001; Corrêa de Sá et al., 1999; Correa and Naique, 1998; Noronha et al., 1992). At Panasqueira, more than 65 minerals including sulphides, sulphosalts, oxides, carbonates, silicates, phosphates, and tungstate minerals, have been identified (Kelly and Rye, 1979). The mine produce wolframite and cassiterite concentrates, with secondary production of copper concentrates. Arsenopyrite (the main sulphide) is rejected to the tailings which contain about 30% of As. The milling facilities at Rio, located near Zêzere River, had the advantage of local ore deposits and water from the river for milling operations (Crosby, 2001). In 1996 the milling operation was transferred from Rio to Barroca Grande. 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 ($\approx 1200000 \text{ m}^3$) 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 arsenopyritic pile (9400 m^3) separated during mill flotation processing (Gilchrist and Mahmoud, 1999 and Crosby, 2001). The mud and slush are discharged into a pond that was intentionally created for that purpose. The pond is an open-air impoundment and contains 731034 m^3 of rejected ore concentrates with high metal levels (Ávila et al., 2008). Infiltration of rain water

occurs across the tailing area, this water carries the acid products of sulphides oxidation. A channel system has been installed to collect the seepage, of acid mine drainage water (AMD), for return to the mill area where a lime treatment neutralises the acidity and endorse precipitation. Precipitates are disposed via pipeline in the mud dam and the neutralised water discharged to the river (Gilchrist and Mahmoud, 1999). During winter and periods of heavy rainfall the system easily overload resulting in mixing of AMD directly with the Zêzere River.

Water Sample Analysis

The surface waters sampling points (Figure 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 (SW1, SW2 and SW3) and one sample from the mine adit at Barroca Grande (SW13). In Rio site, the sampling, include three AMD seepage waters (SW10, SW11 and SW12) and in the main river include two local background waters (SW4 and SW4A), one sample (SW5) after Casinhas stream confluence with Zêzere river and one sample (SW6) from Zêzere but downstream of both tailings areas (Barroca Grande and Rio).

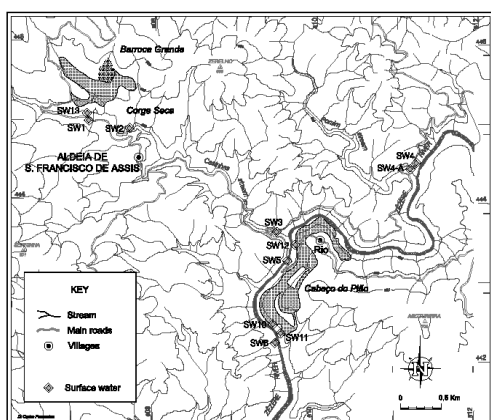


Figure 1 – Sampling location of surface waters

Samples were collected from each site using a clean 1 L acid-washed polyethylene bottle and stored at 4 °C until analysed. Samples for metal analysis were preserved, with pH reduction to 2.0 using HNO₃, avoiding Fe hydroxide precipitation. Temperature, pH, and specific conductivity of the surface waters were recorded at each site. The alkalinity was determined in situ by volumetric titration on filtered unacidified samples using H₂SO₄ acid 0.16 N.

The analyzed elements include major anions, major cations and a suite of dissolved trace metals (Table 1). Ion chromatography and

inductively coupled plasma mass were used to determine the elements concentrations.

Water geochemistry

The results presented in Table 1, shows 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; the Zêzere river waters with 6.8<pH<7.1 and 0.037<SC<0.076 mS/cm and the seepage waters with a 2.9<pH< 3.9 and 1.26 <SC<4.40 mS/cm. These different types of water represent distinct hydrogeochemical processes. The trace-metal concentrations in the seepage waters and waters collected in the Casinhas stream are higher than the concentration in the Zêzere waters. Sulphate concentrations cover a range from 4 to 3717 mg/L 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. The Casinhas stream waters showed higher values of TDS from 227.5 to 707.2 mg/L than those of the Zêzere River which ranged from 24.1 to 49.4 mg/L.

The highest correlation of most other constituents tends to correlate with high sulphate concentrations. Correlation coefficients of data (significance level $p<0.05$) indicate a strong association of $\text{SO}_4^{2-}/\text{Ca}^{2+}$ (0.98); $\text{SO}_4^{2-}/\text{Mg}^{2+}$ (0.99); $\text{SO}_4^{2-}/\text{Na}^+$ (0.93); $\text{SO}_4^{2-}/\text{Al}$ (0.96); $\text{SO}_4^{2-}/\text{Mn}$ (0.98); $\text{SO}_4^{2-}/\text{Fe}$ (0.96); $\text{SO}_4^{2-}/\text{As}$ (0.72); $\text{SO}_4^{2-}/\text{Cd}$ (0.97); $\text{SO}_4^{2-}/\text{Cu}$ (0.98) and $\text{SO}_4^{2-}/\text{Zn}$ (0.98). The strong positive correlation with Ca, possibly, reflects the influence of gypsum and calcite dissolution plus sulphide 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 sulphide 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 (Figure 2). Generally, the seepage and Casinhas stream waters are classified as Mg/Ca-SO₄ 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-HCO₃/SO₄ type.

Table 1 – Physicochemical data of surface waters samples from the Panasqueira area (n=11)

	Casinhas stream			Zêzere river				Seepage waters				
	SW1	SW2	SW3	SW4	SW4A	SW5	SW6	SW10	SW11	SW12	SW13	
pH	-	4.3	5.7	5.7	6.8	7.1	6.9	6.8	3.0	2.9	3.2	3.9
SC	mS cm ⁻¹	0.35	1.09	0.85	0.059	0.037	0.070	0.076	3.63	4.40	2.02	1.26
SiO ₂	mg L ⁻¹	18	16	16	10	12	10	11	103	108	99	30
Cl	mg L ⁻¹	5	7	6	5	4	5	7	5	6	4	5
SO ₄	mg L ⁻¹	152	605	441	4	4	9	12	2990	3720	1400	727
F	mg L ⁻¹	nd	nd	nd	0.11	0.035	0.11	0.18	nd	nd	nd	nd
HCO ₃	mg L ⁻¹	nd	nd	nd	15.3	9.8	14	13.4	nd	nd	nd	nd
PO ₄	µg L ⁻¹	nd	nd	nd	65	65	65	65	nd	nd	nd	nd
NO ₃	mg L ⁻¹	nd	nd	nd	4	1.2	3.9	3.7	nd	nd	nd	nd
NO ₂	µg L ⁻¹	nd	nd	nd	130	5	70	60	nd	nd	nd	nd
Na	mg L ⁻¹	5	12	10.4	6	4	7	7	17.8	19.3	11.8	12.7
K	mg L ⁻¹	1	5	4	1	0.3	1	1	6	0.1	1	2
Mg	mg L ⁻¹	23	73	56	1	1	2	3	274	357	103	95
Ca	mg L ⁻¹	22	120	87	3	1	3	4	287	401	175	107
Al	µg L ⁻¹	1500	800	600	13	7	134	266	149000	161000	99000	6100
As	µg L ⁻¹	5*	13*	13*	2	4	3	4	2140	544	146	48
Cd	µg L ⁻¹	15	58	40	0.2	0.2	0.9	1.6	464	393	226	88
Cu	µg L ⁻¹	190	600	510	6.3	3	42.9	121	42700	54300	20100	2100
Fe	µg L ⁻¹	100	100	290	40	<30	<30	130	82500	91000	9400	1700
Mn	µg L ⁻¹	1100	7000	4100	19	4	85	256	88700	92600	22300	10200
Zn	µg L ⁻¹	2000	6300	4800	18	21	105	181	49200	44500	21900	12400
Li	µg L ⁻¹	32	140	101	<4	<4	<4	4	1170	1010	751	192
Be	µg L ⁻¹	<10	<10	<10	<0.2	<0.2	<0.2	<0.2	57	61	38	<10
Co	µg L ⁻¹	6	84	60	0.3	0.2	3.1	9.6	2620	3330	1140	125
Ni	µg L ⁻¹	110	273	200	<1	1	4	9	2150	2830	1140	397
Sr	µg L ⁻¹	75	338	256	18.3	9	19.9	21.2	658	507	380	396
Y	µg L ⁻¹	6	19	19	0.2	<0.1	0.7	1.3	428	542	322	33
TDS	mg L ⁻¹	228	707	553	38.4	24.1	45.5	49.4	2360	2860	1313	819

* these three values are lower than the quantification limit of the ICP-MS method but higher than the detection limit of the samples. Samples SW1, SW2 and SW3 - Casinhas Stream downstream Barroca Grande tailing; samples SW4 and SW4A - Zêzere river upstream Rio tailing ; samples SW5 and SW6 - Zêzere river; samples SW10, SW11 and SW12 - seepage waters collected in Rio tailing; sample SW13 - mine entrance Barroca Grande; nd - not determined

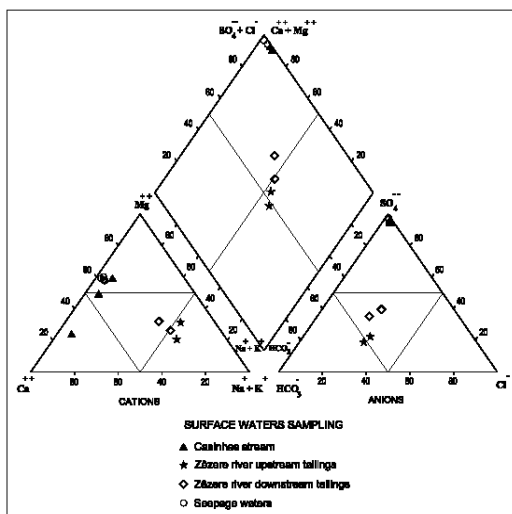


Figure 2 – Piper's diagram of Casinhas stream, Zêzere river and seepage waters samples in the Panasqueira mine area

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 SO₄²⁻ > Ca²⁺ > Mg²⁺ > 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: HCO₃⁻ > Si > Na⁺ > Cl⁻ > SO₄²⁻ > NO₃⁻ > Ca²⁺ > Mg²⁺ > K⁺ and downstream the effects of mining contamination is notorious once the decreasing order of the abundance of major ions is HCO₃⁻ > SO₄²⁻ > Si > Na⁺ > Cl⁻ > NO₃⁻ > Ca²⁺ > Mg²⁺ > K⁺. The oxidation of sulphide minerals in mine-waste rock piles and tailings impoundments generates acidic waters containing high concentrations of SO₄²⁻, 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 sulphate ions but also in some of the major and trace elements.

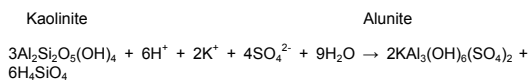
Low-pH conditions promote the dissolution of many metal-bearing solids and the metals desorption from solid surfaces. The probable source of sulphate and heavy metals are the oxidation of sulphide minerals, mainly arsenopyrite, but also pyrite and chalcopyrite. These acidic waters are displaced into 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.

Water rock interaction

Chemical elements speciation was performed using the PHREEQC code (Parkhurst and Appelo, 1999) in conjunction with the WATEQ4F data base (Ball and Nordstrom, 1991). Table 2 shows the saturation index (SI) of the waters with respect to various specified minerals. The SI calculation of the representative minerals in waters show that seepage waters with respect to the silicate minerals 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, kaolinite and montmorillonite, are undersaturated and most of the sulphates, alunite, anhydrite and gypsum, are nearly in equilibrium state in these waters. Regarding Zêzere river waters, according to the calculated SI (Table 2), they are oversaturated in some of the silicate minerals and clay minerals and are undersaturated in sulphates.

The seepage waters are mainly saturated or near equilibrium with respect to alunite $KAl_3(SO_4)_2(OH)_6$ while the majority of the Casinhas stream and the Zêzere River waters are oversaturated in gibbsite $Al(OH)_3$. It is thought that an increase in sulphate activity may promote the formation of sulphate 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.



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

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 (DRX 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 DRX. Acid mine drainage discharged from the Rio tailing (SW10) has a pH of 3.0 and high concentrations of trace metals (Table 1). Also, As concentrations in these samples are high (2138 $\mu g/L$ As). Iron concentration in stream waters decreases rapidly downstream with pH rising. Arsenic concentration decreases downstream with the same pattern of Fe (see sample SW6 - $Fe = 0.13 \text{ mg L}^{-1}$ and $As = 4 \text{ } \mu g \text{ L}^{-1}$). 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).

Conclusions

The present study characterises the Zêzere river hydrogeochemistry on the basis of physico-chemical properties of waters with different locations regarding the tailings: Zêzere river – two samples collected upstream both tailings representing the local background hydrochemistry; two b samples collected downstream 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 characterised 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/sulphate waters. 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 sulphates are nearly in equilibrium state. The Zêzere river waters are oversaturated in some of the silicate minerals and clay minerals and are undersaturated in sulphates. The majority of the Casinhas stream and the Zêzere River waters are oversaturated in gibbsite. An increase in sulphate activity may promote the formation of sulphate 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.

Table 2 – Selected saturation indices (SI) of mineral species for Casinhas stream, Zêzere river and seepage waters from Panasqueira mine area.

Minerals	Casinhas stream			Zêzere river				Seepage waters			
	SW1	SW2	SW3	SW4	SW4A	SW5	SW6	SW10	SW11	SW12	SW13
Albite	-6,65	-2,11	-2,42	-3,21	-3,21	-2,23	-1,64	-8,05	-8,51	-7,19	-7,30
Alunite	1,51	7,87	7,19	-5,11	-7,97	-0,55	1,17	-0,51	-3,06	0,15	0,66
Anhydrite	-2,10	-1,07	-1,27	-5,18	-5,57	-3,92	-3,71	-0,51	-0,35	-0,83	-1,09
Calcite	nc	nc	nc	-2,94	-3,32	-2,89	-2,88	nc	nc	nc	nc
Chalcedony	0,03	-0,02	-0,02	-0,16	-0,10	-0,21	-0,15	0,79	0,82	0,77	0,25
Chlorite	-36,02	-14,61	-15,96	-14,88	-13,15	-11,77	-10,32	-49,15	-50,84	-46,57	-40,18
Dolomite	nc	nc	nc	-5,89	-6,11	-5,63	-5,63	nc	nc	nc	nc
Fluorite	nc	nc	nc	-4,10	-5,41	-4,11	-3,55	nc	nc	nc	nc
Fe(OH) ₃	-6,89	-3,17	-2,55	0,22	0,44	-0,08	0,85	-8,33	-8,71	-8,40	-7,21
Gibbsite	-0,17	2,80	2,61	1,52	1,06	2,33	2,78	-3,00	-3,42	-2,17	-1,38
Gypsum	-1,88	-0,85	-1,05	-4,95	-5,33	-3,70	-3,48	-0,29	-0,13	-0,61	-0,87
Halloysite	-3,66	2,17	1,79	-0,71	-1,50	0,85	1,85	-7,78	-8,59	-6,17	-5,64
Kaolinite	1,40	7,23	6,85	4,39	3,61	5,91	6,96	-2,72	-3,53	-1,11	-0,57
Kmica	0,14	11,01	10,28	7,27	5,69	9,64	11,17	-6,59	-9,70	-4,54	-2,87
Montmorillonite Ca	-1,35	5,93	5,45	2,52	1,72	4,29	5,57	-5,44	-6,38	-3,53	-3,42
Quartz	0,46	0,41	0,41	0,28	0,34	0,22	0,29	1,22	1,25	1,20	0,68

nc - not calculated; positive saturation indices are in bold

References

- Ávila, P.F., Ferreira da Silva, E., Sagueiro, A. R., Farinha, J. A., 2008. Geochemistry and mineralogy of mill tailings impoundments from the Panasqueira Mine (Portugal): Implications for the surrounding environment. *Journal of International Mine Water Association*, Vol. 27, Issue 4, pp. 210-224.
- Ball, J.W., Nordstrom, D.K., 1991. User's manual for WATEQ4F, with revised thermodynamic database and test cases for calculating speciation of major, trace and redox elements in natural waters. U.S. Geological Survey Open-File Report 91-183, 189p. (Revised and reprinted August 1992).
- Blowes, D.W.; Ptacek, C.J.; Jambor, J.L. Weisener, C. G., 2003. The Geochemistry of Acid Mine Drainage. *Treatise on Geochemistry Volume 9*, pp. 149–204.
- Breiter, K., 2001. Report about Laboratory Investigations of Rock Samples from the Panasqueira Mine and Recommendations for Future Exploration, Nov 2001.
- Correa, A.; Naique, R.A., 1998. Minas Panasqueira, 100 Years of Mining History. Paper presented at the 1998 International Tungsten Industry Association (ITIA) conference.
- Corrêa de Sá, A.; Naique, R.A., Nobre, E., 1999. Minas da Panasqueira – 100 anos de História. *Bol de Minas* 36 (1): 3-22 (in portuguese).
- Crosby, T.W., 2001. Facility Environmental Review, Beralt Tin and Wolfram Portugal SA, by SECOR International Incorporation.
- Dove P.M., Rimstidt J.D., 1985. The solubility and stability of scorodite, FeAsO₄.2H₂O. *Amer. Mineralogist*: 70, 838-844.
- Gilchrist, H.G., Mahmoud, M., 1999. Final Report, A Subjective Evaluation of Tailings Deposits Stability at Panasqueira Mine, Portugal, by Golder & Associates.
- Inoue, A., 1995. Formation of clay minerals in hydrothermal environments. In: Velde, B. (Ed.), *Origin and Mineralogy of Clays*. Springer, Berlin, pp. 268–330.
- Jambor, J.L.; Blowes, D.W., Ritchie, A.I.M. 2003. *Environmental Aspects of Mine Wastes. Mineralogical Association of Canada, Short Course Series, vol. 31, 430p.*
- Kelly, W.C., Rye, R.O., 1979. Geologic, fluid inclusion and stable isotope studies of the tin-tungsten deposits of Panasqueira, Portugal. *Econ Geol* 74: 1721-1822.
- Nordstrom, D.K., Wright, W.G., Mast, M.A., Bove, D.J., Rye, R.O., 2007. Aqueous-sulfate stable isotopes - A study of mining-affected and undisturbed acidic drainage, in Church, S.E., von Guerard, P., and Finger, S.E., eds.: U.S. Geological Survey Professional Paper 1651, chapter E8, p. 387-416.
- Noronha, F.; Doria, A.; Dubessy, J. and Charoy, B., 1992. Characterization and timing of the different types of fluids present in the barren and ore veins of the W-Sn deposit of

- Panasqueira, Central Portugal. Miner Deposita 27: 72-79.
- Parkhurst, D.L. and Appelo, C.A.J., 1995. User's guide to PHREEQC (version 2). A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312p.
- Perry, W.T.; Ballantyne, J.M.; Bryant, N.L. and Edolph, R.E., 1980. Geochemistry of hydrothermal alteration at the Roosevelt Hot Springs thermal area, Utah, Geochim. Cosmochim. Acta **44**, pp. 95–102.
- Plumlee, G.S. and Logsdon, M.J. Editors, 1999. The Environmental Geochemistry of Mineral Deposits: Part A. Processes, Techniques, and Health Issues, Rev. Econ. Geol. **vol. 6A**, 371 p.
- Reis, A.C., 1971. As Minas da Panasqueira. Bol Minas 8 (1), pp.3 – 34 (in portuguese).
- Wirsching, U., Ehn, R., Holler, H., Klammer, D., Sitte, W., 1990. Studies on hydrothermal alteration by acid solutions dominated by SO_4^{2-} : formation of the alteration products of the Gleichenberg latitic rock (Styria, Austria) - experimental evidence. Mineral. Petrol. 41, pp.81 – 103.