GEOCHEMICAL SIGNATURE OF MINING INDUSTRY IN THE SURROUNDING ENVIRONMENT OF PANASQUEIRA MINE (PORTUGAL)

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Abstract

e-Ecorisk project (http://www.e-ecorisk.info/) is an EU 5th Framework Programme and it was developed to create an information management network and a system to support decision-makers. Through the application of advanced and innovative information and communication technology, this project provides information on potential and actual risks of large-scale industrial spills into the environment and to the society. e-Ecorisk is designed to identify, characterise and quantify the threat and potential environmental and social impacts (harm) of a catastrophic disruption of an impoundment which would lead to the uncontrolled release of effluent into the environment (e-EcoRisk, 2001). e-Ecorisk project intends to perform the physical, chemical and mineralogical characterisation of stored mining leftovers present not only in tailing ponds but in the surrounding area as well.

The Panasqueira mine is one of the Portuguese test-sites to be studied in the scope of e-Ecorisk project. This study will be centred both in the arsenopyrite-rich mining leftovers that are disposed into two large tailing sites (Rio Tailings ≈ 5MT and Barroca Grande tailing ≈ 17MT) and in the ore processing materials stored in open-air impoundments which are responsible for the continuous generation of acid drainage.

Introduction

It is known that mining industry may cause negative impacts in its surrounding area. These consequences can become particularly worrying whenever the exploitation and ore treatment operations are performed in the vicinity of villages. Soils and waters can be easily contaminated by metals (and metalloids) due to their direct contact (and interference) with the chemical processes of metal liberation and mobilisation that commonly result from mining operations (Alloway, 1993; Forstner and Wittmann, 1983). Mine wastes containing high sulphide concentrations are among the most serious sources of environmental pollution. Understanding the geochemical processes which control precipitation and dissolution of secondary minerals in abandoned sulphide mines is crucial for the elaboration of models which predict the environmental impact of such sites (Gieré et al., 2003). A better knowledge of these geochemical mechanisms will allow the remediation of existing problems and will help the e-ecorisk consortium to alert authorities whenever a spill occurs.

The Panasqueira Sn-W mine is located in Central Portugal and was chosen as an e-EcoRisk test site due to several factors: it's an active mine, there are large tailing areas and dams, small villages around the mine site are present, and there is the Zêzere river which crosses the area and feeds the Castelo do Bode dam, the main source of water supply to Lisbon. The Panasqueira mine began its activity in 1896 and the Rio area consists of a large site where tailings and a treatment system are present. The milling operations ended in 1996, when this site was relocated to Barroca Grande. For approximately 90 years tailings were disposed in the Rio site. The existing pond on the top of the Rio tailing site, is an open-air impoundment and contains 731034 m^3 of rejected ore concentrates with high content in metals.

The present study shows selected geochemical results obtained in Panasqueira area; the aim was to better understand the dynamics inherent to leaching, transport and accumulation of some elements with environmental relevance (mainly As, but also Cu, Pb, Zn and Cd) in different sampling media.

Geological setting and mineral paragenesis of Panasqueira mine

The Panasqueira ore deposit is the biggest wolframite ore body of the Western Europe and a classical example of Sn-W hydrothermal mineralization associated to Hercynian plutonism. According to the paleogeographic and tectonic zoning established for the Hercynian Chain of the Hesperic massif (Lotze, 1945; Julivert et al., 1974), this deposit is included in the Central Iberian Zone. Folded metasediments of Cambrian to late Precambrian age showing low-grade metamorphism outcrop in the area which is intruded by Hercynian granitoids. Near the contact, metasediments grade to spotted schists, due to processes of contact metamorphism which can be observed in lithologies around the mining site (Conde et al., 1971; Bloot and de Wolf, 1953; Kelly and Rye, 1979). Outcrops of spotted schists were identified around the mining site (Fig. 1), and are spatially associated with most of mineralization. The mineral deposit is hosted in metasediments where a great number of subhorizontal quartz veins rich in ferberite are present. Wolframite, cassiterite and chalcopyrite are also comprised in the mineralisation. Certain sulphides and carbonates such as arsenopyrite, bismuthinite, galena, sphalerite, pyrrothite, marcassite and stannite are the most important accessory minerals. Other minerals like calcocite, covellite, cubanite, loellingite, molibdenite, pentlandite, stibnite and silver sulphosalts occur in minor amounts. The economic exploitation has been mainly focused on wolframite, cassiterite and chalcopyrite.

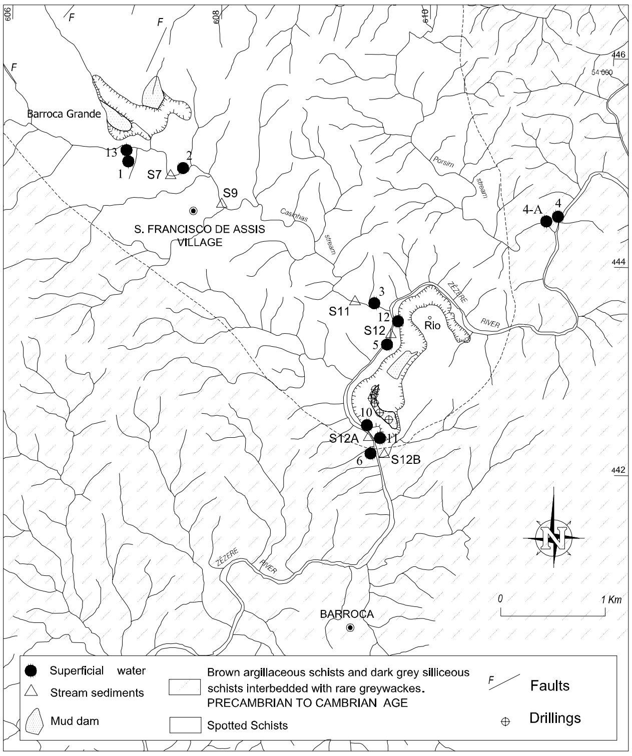

Figure 1. Study area with local geology and location of sampling points.

Tailings and dams

The Rio tailing site, located nearby the Zêzere River draining directly this site, is characterised by an average height of 90 meters from the base to the top, and has slopes of about 35º. The grain size of the materials is variable, due to successive finer grinding procedures. These leftovers are classified as: coarse sterile material from the mine; coarse tailings (sterile material) from the heavy media separation; sand; mud and slush. The three first types of materials are disposed in tailings, while mud and slush are discharged in a pond located in the SE top of the tailing site, specifically created for that purpose (e-Ecorisk, 2004). In Rio tailing area there is an arsenopyrite stockpile located very close to slope. This stockpile shows several sliding zones and also acid drainage. In this scenario, the arsenopyrite pile represents a hazard: it could be transported to the Zêzere River by impoundment disruption.

Presently these operations are being carried out exclusively in Barroca Grande where the existence of a tailing and two mud ponds must be emphasised. One of them is an old stabilized impoundment (in geotechnical terms), while the other (smaller and disposed over the tailing) is being feed with materials obtained from the ore dressing operations (e-Ecorisk, 2004).

Tailings and impoundments exposed to the atmospheric conditions for long periods tend to be affected in their chemical, mineralogical, physical and geotechnical characteristics. Climate, which can be an important instability factor, is aggressive in the Panasqueira region with hot and dry conditions during summer, and very cold, rainy and windy in the winter. Surface runoff and percolation of precipitation are responsible for the leaching of the tailing materials and formation of acid drainage. To prevent these processes, wastewaters are collected, pumped and treated in two water treatment plants (located in Rio tailing site and in Barroca Grande). Acid effluents are neutralised with lime $Ca(OH)_2$, which promotes metal precipitation and flocculation when pH increases. After this treatment, clean water is returned to the ore dressing plant, or discharged directly in the Zêzere river.

Methodology and analytical techniques

In order to assess the dynamics of leaching, transport and accumulation of some selected metals and metalloids, different sampling media (stream sediments, impoundment materials, coatings, arsenopyrite stockpile material, ferruginous crust existing in Rio tailing site and stream waters) were collected (Fig. 1). The impoundment material was sampled on 6 drill cores undertaken by IGM (Instituto Geológico e Mineiro) in 2002 (Dinis da Gama, 2002). The core logs revealed that upper parts are generally formed of fine dark grey mud while the lower parts have reddish colours. The sections with muds and ferruginous crusts are related to successive dry summers in the past.

A total of 17 samples were collected on the cores. The solid materials were dried at 40°C and sieved at 80 mesh, crushed, homogenized and again sieved, retaining the <200 mesh fraction for chemical analysis. The fine-grained fraction was submitted to multielement chemical analysis, in S. Mamede de Infesta INETI accredited Lab, by DCP. The surface waters were filtered and preserved with HNO_3 acid. The samples were stored under cool and dark conditions prior to analysis by Ionic Chromatography and ICP-MS.

Results and Discussion

The arsenic concentrations in the cores taken in the pond show two distinct zones within the mud body: to a depth of 17 m As contents ranges from 5% to 24%, and below this depth the As concentration decreases to values near or below 1%. This variation may be associated with the beginning of copper recovery in the 1970s. The impoundment material shows high contents in As, Cd, Cu, Pb and Zn (average contents: As = 73649 mg/kg; Cd = 1227 mg/kg; Cu = 2497 mg/kg; Fe = 12.5%; Mn = 924 mg/kg; Pb = 215 mg/kg and Zn = 6843 mg/kg). This dam is an open impoundment and consequently the sulphides (arsenopyrite, pyrrothite and chalcopyrite) were oxidized producing secondary minerals as scorodite and natrojarosite (mineralogical composition of the <63 µm and <2 µm fractions analysed by X-ray diffraction). According to Salzsauler et al. (2005) these secondary minerals will attenuate the As release to the water during oxidation.

The results from surface water analysis (Table 1) reveal low concentrations of chloride and, some of them, high sulphate contents (samples 2 and 3). In Barroca Grande, the water treatment with lime $Ca(OH)_2$ increases the pH and reveals his efficiency in iron removal from waters, through its precipitation and simultaneously the co-precipitation of As and Cu with Fe (samples 1, 2 and 3 collected after Barroca Grande water treatment plant).

Table 1. pH, conductivity (µS/cm), major ions (mg/L) and trace elements (µg/L) in surface waters.

Samples	1	2	3	4	4A	5	6	10	11	12	13
pH	4.3	5.7	5.7	6.8	7.1	6.9	6.9	3.0	2.9	3.2	3.9
Cond.	350	1088	851	59	37	70	76	3630	4400	2020	1260
Cl^-	4.6	6.7	6	5.2	3.9	5	6.7	5.3	6.7	3.6	4.6
SO_4^{2-}	152	605	441	4.1	3.5	9.2	12.2	2991	3717	1398	727
Na^+	5.2	12	10.4	6.4	4.2	6.5	6.5	17.8	19.3	11.8	12.7
Ca^{2+}	22.3	120	87	2.6	1.2	3	3.9	287	401	175	107
Fe	100	<100	290	40	<30	<30	130	82500	91000	9400	1700
Al	1500	800	600	13000	7000	134000	266000	149000	161000	99000	6100
Mn	1.1	7	4.1	19.3	3.5	84.6	255.9	88.7	92.6	22.3	10.2
Cu	0.19	0.6	0.51	6.3	3	42.9	120.8	42.7	54.3	20.1	2.1
Zn	2	6.3	4.8	18	21	105	181	49.2	44.5	21.9	12.4
As	5	13	13	2	4	3	4	2138	544	146	48
Cd	15	58	40	0.2	0.2	0.9	1.6	464	393	226	88
Pb	<22	<22	<22	<0.3	<0.3	<0.3	<0.3	<22	<22	<22	<22

The seepage water samples (10, 11 and 12) show pH values between 2.9 and 3.2. The regional hydrochemical facies is Na-Cl type but changes occur to $Ca-SO_4$ facies nearby the mining influence. These results indicate that leaching is taking place, as the Zêzere River hydrochemistry downstream Rio tailing site shows high concentrations of Al, Zn, Mn and SO_4^{2-} (samples 5 and 6). However, these samples do not reveal high As concentrations, mainly due to the co-precipitation with Fe (III) oxyhydroxides in the tailing basement. Arsenic can also be removed from the solution and precipitate as scorodite. This mineral is the most common iron arsenate associated to arsenic deposits as a leaching product. Its presence controls the arsenate levels in waters draining As-rich ores. Scorodite formation involves arsenopyrite oxidation at low pH and high iron and arsenate activity, and it only dissolves with increasing pH, meaning As contents are kept low while solution's pH is still low (Dove and Rimstidt, 1985).

The sample collected in the arsenopyrite stockpile from Rio tailing site shows high concentrations of As, Cd, Cu, Fe, Mn, Pb and Zn (As = 120000 mg/kg; Cd = 3057 mg/kg; Cu = 1426 mg/kg; Fe = 19.8%; Mn = 410 mg/kg; Pb = 1450 mg/kg and Zn = 460 mg/kg). The seepage water collected at the basement of the arsenopyrite stockpile in this site shows high conductivity, and also high concentrations in trace metals (Table 1), revealing that metals are suffering continuous leaching originated from the sulphides oxidation which is taking place in those tailings.

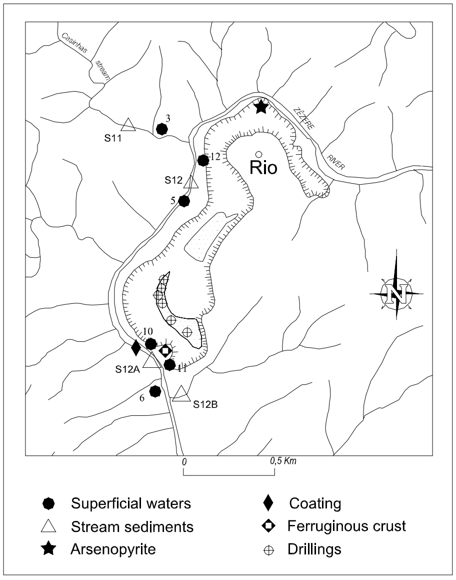

Figure 2. Rio tailing site with the location of selected sampled media.

One sample of an iron precipitate (coating) was collected in the main river nearby water samples 10 and 11. The coatings formation is due to the pH increase, verified when seepage waters, with high levels of dissolve iron, mix with the more oxygenated river water (Carpenter et al., 1975).

Comparing the chemical results of the coating sample (As = 37000 mg/kg; Cd = 423 mg/kg; Cu = 1626 mg/kg; Fe = 25.1%; Mn = 712 mg/kg; Pb = 139 mg/kg and Zn = 1288 mg/kg) and the water sample 6 collected nearby (Fig. 2 and Table 1), it seems that the decrease of heavy metal contents in water sample, namely As, Cu and Cd, is associated to the co-precipitation with Fe and Mn oxides influenced by pH increment. The ferruginous crust also reveals high contents of Fe, Cu, Zn, Cd and As (As = 40000 mg/Kg; Cd = 453 mg/Kg; Cu = 3305 mg/Kg; Fe = 12%; Mn = 572 mg/Kg; Pb = 319 mg/Kg and Zn= 663 mg/Kg) and confirms the transfer of these elements from the tailing and mud impoundment. The presence of melanterite was also observed in Rio tailing basement. According to Frau (2000), the precipitation and dissolution of such secondary minerals are processes strongly influenced by seasonal wetting and drying cycles.

Table 2 shows selected water and stream sediment samples collected in the Casinhas stream and Zêzere River.

Table 2. Comparison of surface waters and stream sediment data in three samples collected in the Casinhas stream and Zezere river in the same place (waters in µg/L and stream sediment in mg/kg).

	pH	Conductivity	As	Cu	Pb	Zn	Cd	Fe
Water 2	5.7	1088	13	0.6	<22	6.3	58	<0.1
Stream sed.7	-	-	18000	4561	117	3562	268	81000
Stream sed.9	-	-	17000	2994	66	2259	247	73000
Water3	5.7	851	13	0.51	<22	4.8	40	0.29
Stream sed.11	-	-	6000	3166	31	2705	112	59000
Stream sed.12	-	-	15000	895	83	247	186	48000
Water 6	6.9	76	4	120.8	<0.3	181	1.6	0.13
Stream sed.12A	-	-	1489	620	18	199	18	40000
Stream sed.12B	-	-	212	402	33	304	2	35000

Results on the water treatment plant show that iron is removed from waters due to its precipitation and also through the co-precipitation of As and Cu with Fe, probably adsorbed on the stream sediments. Comparing the As, Cd, Cu, Zn and Fe results of samples 2 and 3 for water and stream sediments, it is evident the high accumulation level of these metals in the stream sediments.

Conclusions

This research was carried out in order to identify the anomalous distribution of some heavy metals in the tailing ponds and to understand the mobility and transfer mechanisms to the secondary geochemical environment. The main conclusion is that the tailings and impoundments are the main source of pollution in the surrounding area. However, the role of secondary minerals controlling the metals migration to waters is relevant.

Oxidation of sulphides can result in the mobilization and migration of trace metals from the mining wastes into the environment, releasing the contaminants to the ecosystem. The mining and beneficiation processes in the Panasqueira produce arsenic-rich mine wastes responsible for the high levels in this element at the Panasqueira mining site.

Stream sediments appear to be a good receptor of the majority of metals and water seems to be the most important mean responsible for metals leaching, confirmed by high chemical contaminations in samples under mining influence.

Secondary minerals play an important role in the natural retention of oxyanions ($H_2AsO_4^-$) and divalent cations (Cu, Zn and Pb) due to the elements capture by sorption and precipitation.

The results probably show that the water treatment plant that exists in Rio site is not working efficiently, as it is evident the presence of high levels of Cu, Zn and some Cd in Zêzere River.

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