Geochemistry of Soils and Waters from the Abandoned Freixeda Gold Mine, Northeast Portugal

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INTRODUCTION

Freixeda mine is located in NE Portugal, near Mirandela city, and was exploited for Au, Ag and Pb until 1955. The mine was closed after 1995 and more than 0.5 million tons of tailings remained exposed to erosion for more than 50 years. In the year of 2007 environmental recovery was pursuit and tailings were sealed and galleries closed.

Several studies on environmental impact of Freixeda mine on soils, surface water and groundwater were developed in the last 10 years. Some results will be presented and interpretation to explain the very high concentration of Arsenic in soils, groundwater and in surface water will be proposed.

GEOLOGICAL SETTINGS

Freixeda Mine is part of the Gold-Silver Metalogenetic Province of Iberian Peninsula. These gold and silver deposits are usually associated with Paleozoic quartzits (Ordovician age) and with black schists (Ordovician and Silurian age) and not so often they can be intragranite. Gold ocurrences are associated with veins, stockwerks and silicified masses in metamorphic metasediments, afected by shear zones, thrusts and latter fractures and faults from Variscan Orogeny.

At Freixeda mineralization is present in quartz veins installed in the phylitic-quartzitic Formation. These veins belong to a system of parallel to subparallel structures filled with quartz highly crushed and impregnated with sulfides occupying numerous fractures and micro fractures (Parra and Lopes 1999). According to Almeida and Noronha 1988, the mineral deposition sequence has to steps of mineralization: the first is characterized by the association of scheelite + wolframite + sulfides (mainly arsenopiyrite, pyrite, pirrotite and molibdenite) and can be found at Pedra da Luz, south of Freixeda; the second, is characterized by the association of chalcopyrite + sphalerite + sulphosalts + galena + native elements, and is well represented at Freixeda. These authors assume that these two steps belong to the same mineralization process with deposition of quartz during the deposition of the other minerals.

FREIXEDA MINE MINERALOGY AND SOILS GEOCHEMISTRY

Mineralogy of quartz veins at Freixeda are silicate minerals – mainly quartz and chlorite – and sulfide minerals - arsenopyrite (the most abundant) pyrite, sphalerite, galena, chalcopyrite and As, Pb, Fe and Sb sulphosalts. Arsenopyrite has the general formula FeAsS but some As was replaced by Sb and pyrite has some As in it's composition reaching 1.74%. Jamesonite and rayite are the most frequent sulphosalts present.

Soils sampled in the region show higher variation in As and Pb content (*Table 1*). Spatial distribution of As, Pb, Ag and Sb are shown in *Figure 1*. It can be observed in this figure that the highest anomaly values for the four elements are associated with soils in the vicinity of tailings. Arsenic in particular has a more disperse area with values of more than 1000 mg/kg. These maps show large areas with soils inappropriate for agriculture due to concentration above admissible values. According to Environmental Canadian quality guidelines Arsenic in soils shouldn't surpass 12 mg/kg for agriculture, residential or industrial use.

	As	Cr	Cu	Pb	Zn	Ag	Sb
Minimum	6	12	8	18	65	<0,1	0.9
Maximum	7663	118	395	1000	1247	95	640

Tabla 1. Maximum and minimum values, in mg/kg, found in soils from Freixeda region. 516 soil samples.

HYDROGEOCHEMISTRY

Water samples were collected in 2004 and 2007 from the outflow of a gallery with acid mine drainage, and from groundwater and surface water, upstream and downstream from the mine influence at Ribeira de Freixeda watershed.

ACID MINE DRAINAGE (AMD)

AMD has 3.5 <pH< 4.2 and is Mg-SO_4 type with high concentration of Al (1.01 mg/L), Fe (5.22 mg/L), Mn (10.1 mg/L), SO_4 (369 mg/L) and low As concentration (18 µg/L). Electrical conductivity (EC) is around 600 µS/cm.

SURFACE WATER

Water from Ribeira de Freixeda upstream from the AMD confluence is not affected by the mineralization and has

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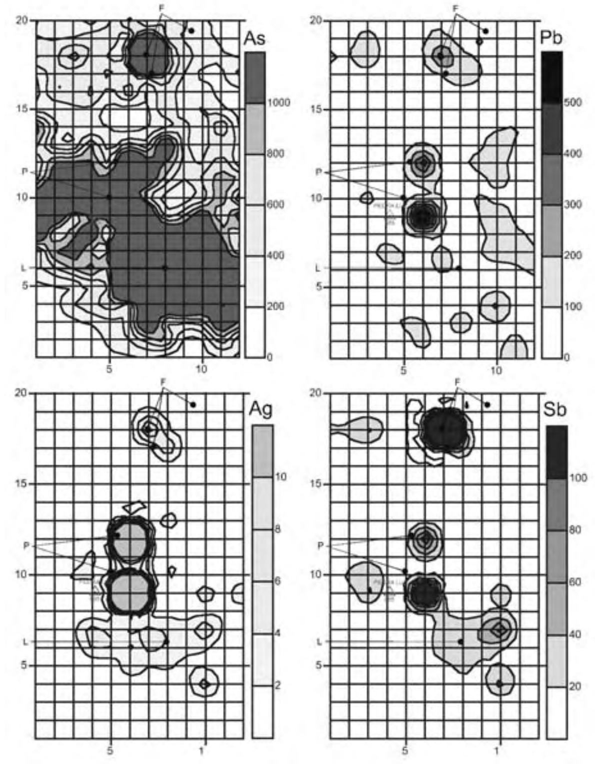

Fig. 1. Distribution of As, Pb, Sb and Ag in soils (mg/kg) of Freixeda region. Gride has 200 meters per side. F – Freixeda tailings; P – Pedra Luz tailings; L – Lombo Veiga tailings.

$Ca\text{-}HCO_3$ type, slightly basic pH with no detectable As and no significant concentration of trace metals. Downstream from the AMD, surface water becomes $Ca\text{-}Mg\text{-}SO_4$ type with elevated concentrations of As (190 µg/L), Zn (660 µg/L) and Mn (111 µg/L). Fe is not in solution.

GROUNDWATER

Groundwater from a spring outside the influence of the mine has a pH of 6.5 and is of $Ca\text{-}Na\text{-}HCO_3$ type with no anomalous trace element concentration and EC of 200 mS/cm. Groundwater exploited from a deeper well near the mine is of $Mg\text{-}SO_4$ type, pH is about 6.5 and has much higher EC (700 µS/cm) and high concentration of As (497 µg/L), Mn (9.51 mg/L) and Fe (5 mg/L). This well is overflowing during all the year, and during driest years (as 2007 for example) Freixeda stream was dried and it was possible to see the discharge from the aquifer into the stream from the left margin. Outside the well casing there's a reddish precipitate. The chemical analysis of this precipitate, collected in July 2007 point to precipitation of oxides of iron and manganese with adsorbed arsenic what should happened when groundwater gets in contact with oxygen (*Table 2*).

WATER-ROCK INTERACTION REACTIONS

Water geochemistry is strongly affected by sulfide oxidation reaction. This reaction releases cations, SO_4^{-2} and H^+ ions. Free H^+ ions contribute to the dissolution of carbonates (present in cement of metasedimentary rocks) and to the hydrolysis of silicate minerals (plagioclases) promoting the alkalinity and pH increase.

Inverse geochemical modeling was used in order to identify water-rock interaction processes that control the geochemical evolution of groundwater (Pereira and Almeida 2000).

The mass balance calculations were made with NETPATH (Plummer et al. 1992). The plausible phases were selected according to the mineralogical composition of the local rocks and the results of chemical speciation.

The selected geochemical inverse model is:

1st Pyrite oxidation by O_2, in open system, with precipitation of goethite
2nd Plagioclase dissolution, with kaolinite and silica precipitation
3rd Calcite and dolomite dissolution
4th Soil carbon dioxide dissolution
5th Ionic exchange Ca^{+2}/Na^{+}

Oxidation of pyrite, needs an elevated quantity of oxygen to occur which means that it should happen in an open system. This reaction is responsible for the high content in sulfate and, as a proton donor, promotes the dissolution of silicates (with precipitation of kaolinite and silica) and carbonates.

Concentration of As in surface water is much lower than in groundwater probably do to adsorption of As on Fe oxyhydroxides, that precipitates in stream sediments while in groundwater, the low oxidation-reduction potential and higher pH conditions, that allow Fe and Mn to remain in solution, could be responsible for the higher As concentration. This interpretation is supported by the absence of dissolved iron in surface-water samples.

	As	Fe (%)	Mn	Cd	Zn	Be
Precipitate	410000	46.4	25000	471	399	66

Tabla 2. Analytical results, in mg/kg, from the chemical analysis of the precipitate in the out flowing well near Freixeda mine. Units are in mg/kg.

Discharge from the confined aquifer to the stream flow can be responsible for As concentration higher than 200 µg/L in Freixeda stream.

CONCLUSIONS

Arsenic contamination in soils and water resources is widespread in the region and it is the main contaminant.

Arsenic in soils reaches values higher than 1000 mg/kg in areas larger than one kilometer far from tailings.

Surface water bellow mine influence in Ribeira da Freixeda is affected by acid mine drainage and also by aquifer discharge to the stream flow and it's not suitable for human consumption or irrigation in particular due to Arsenic concentration that can reach about 200 µg/L.

Groundwater represents a threat to human health due to the high concentration in As (reaching about 500 µg/L) and Mn (> 9 mg/L).

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