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An integrative assessment of environmental degradation of Caveira abandoned mine area (Southern Portugal)

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ABSTRACT

Since the end of the 1990s the Portuguese Iberian Pyrite Belt (IPB) is a typical European post-mining region with significant problems related to acid mine drainage (AMD), metal dispersion, mine waste management and unsafe mining infra-structures. The Portuguese government is providing particular attention on the sulphide abandoned mines and doing considerable investments on the mining recovery all over the country.

The former Caveira mine was closed in the 1980s. It is considered an extremely impacted site due to the dimension of the areas affected by mining activities. Tailings, mine addicts and associated waste rock dumps, resulting from 129 years of pyrite and Cu exploitation, are spread along the Grândola stream. Despite the semi-arid climatic conditions of the area, the tailings are considerably eroded by the surficial waters, particularly during rainfall events.

The past mining and smelting activities have resulted in severe contamination of the Grândola stream and its tributary by AMD (pH < 2) as well as degradation of surrounding stream sediments, soils and vegetation. In order to evaluate possible environmental risks, a sediment and surface water survey was carried out downstream the Caveira mine. The acidic effluent and mixed stream water show high Al, As, Ca, Cd, Cu, Fe, Hg, Mg, Mn, Ni, Pb and SO_4 concentrations, with several of these contaminants exceeding local and/or surface water quality standards. The data show a strong seasonal variation of surface water quality with poorer water quality during the dry and rainy seasons caused by evaporation and efflorescent salt dissolution, respectively. The variable flow regime at the local streams causes dilution of AMD rich in trace metals reaching background within 14 km downstream. The potential toxicity of stream metal concentrations was determined using cumulative criterion unit (CCU) scores and the modified AMD index (MAMDI), which highlighted As, Cd, Cu, Pb and Zn as the major sources of potential chronic stream toxicity, with emphasis on winter season. Although the threshold of the likely harm to aquatic life is exceeded at all sites, the two indexes highlight differences relating to the extension of contamination effects. The Average Index of Toxicity (AIT) showed that sediment contamination is very high even when the distance to mine promoted a decreasing in water metal concentrations, which are being precipitated in the sediments due to pH increase.

1. Introduction

The Iberian Pyrite Belt (IPB) is known as a mining district of worldwide significance, due to the unusual metal sulphide concentration of its large and medium sized mineral deposits. Mining activity in this district dates back to the Roman times and was an important sector of the Portuguese economy during the 19th and the first half of the 20th centuries. The majority of the mining activity ceased due to the ore exhaustion and to the introduction of new and more profitable techniques elsewhere, reducing the ore prices, which made the extraction of these mines unviable (Martins and Oliveira, 2000).

Sulphide ore mines produce huge amounts of waste material that is often rich in pyrite and other sulphides. The exposure of these sulphur-bearing minerals to the air and water promotes their oxidation and hydrolysis leading to sulphuric acid production, which is enhanced by the high reactive surface promoted by the mill processes. This situation is worsened due to the mine abandonment, associated with a lack of maintenance of tailings and waste dumps. In some cases, the occurrence of tailing impoundment disruptions has caused the discharge of potential harmful materials and the consequent contamination of soils and waters.

Pyrite, one of most abundant sulphide minerals, may be oxidised by biotic and abiotic processes. Sulphate, Fe and H^+ are released into solution forming what is commonly known as acid mine drainage (AMD) (Bigham and Nordstrom, 2000; Jönsson et al., 2006). The

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oxidation reaction process of pyrite can be generalized by the following equations:

$$FeS_{2(s)} + \frac{7}{2}O_{2(aq)} + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + \frac{1}{4}O_{2(aq)} + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O \quad (2)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+ \quad (3)$$

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+. \quad (4)$$

By Eq. (1), pyrite is oxidized, thereby releasing Fe^{2+}, SO_4^{2-} and H^+. Ferrous iron can be oxidized to Fe^{3+} in an acid consuming reaction (Eq. (2)). The low rate of this reaction in acidic conditions is overcome by the occurrence of acidophilic bacteria that greatly enhances the Fe^{2+} oxidation (Singer and Stumm, 1970). Ferric iron can then either be hydrolysed and form ferric hydroxide [$Fe(OH)_3$] and H^+ (Eq. (3)), or it can directly oxidize pyrite, acting as a catalyst, leading to the generation of Fe^{2+} and SO_4^{2-}, and high acidity (8 times higher than oxidation of pyrite by O_2) (Eq. (4)). Actually, Fe^{3+} is the only effective oxidizer of pyrite in acidic conditions (Singer and Stumm, 1970). The ferric hydroxides, formed by Fe^{3+} hydrolysis, precipitate as ochre coatings on stream beds affected by AMD and can also coat the pyrite surface preventing its oxidation. Thus, the AMD extent impact on the stream waters may depend on the pyrite content and its oxidation rate (Kim et al., 2003).

AMD has environmentally significant consequences by the high acidity, the leaching of toxic metals from wastes and their spread in the environment, affecting the delicate and highly vulnerable aquatic systems (Chapman et al., 1983; Herr and Gray, 1996; Protano and Riccobono, 2002). The AMD with high concentration of SO_4, Fe, Al and Mn shows pH values near 2 or lower (Chon et al., 1999; Nordstrom et al., 2000). From an ecotoxicological point of view, greater attention has traditionally been paid to hazardous elements such as As, Cd, Cu, Hg and Pb, whose adverse effects on life are well established. The dissolved species of these elements may precipitate in the stream bottom under control of the chemical conditions from streams.

This study was intended to investigate and quantify the disturbances that occur in the surrounding environment of the abandoned sulphide mine of Caveira, on the basis of geochemical content and behaviour in the stream sediments and surface waters as the main receptors. In addition, the impacts of trace elements and AMD in biota were estimated. Considering that mining environmental impacts are site specific, the characterization and the understanding of these local contamination processes are crucial in the definition of an environmental remediation plan of the mining area.

2. Study area

2.1. Geographical and geomorphological setting

The Caveira mine is located in the NW extreme limit of the IPB, in the south of Portugal (Alentejo), and belongs to the Grândola municipality (Fig. 1). This is an abandoned sulphide mine, where mining focused mainly in the pyrite exploitation for sulphuric acid production. The degradation of the old mining quarters and the non-natural hill formed by the tailing deposits cause a striking visual impact in the landscape.

The geomorphology of the region is characterized by smooth reliefs, strongly controlled by the WNW–ESE major Grândola active fault. Close to the main streams the relief is moderate with slopes ranging from to 2 to 5%, whereas the neighbouring hills are dominated by long steep slopes (10%–35%) and intensely forested with eucalyptus. Since the mine closure, human occupation is very limited, where cereal agriculture (only in the northern sector) and forest are the main local land use.

The watercourses in the vicinity of the mining area belong to the Sado watershed, which shows a median slope of about 4%. The main watercourse of the region is the Sado river, with a length of 176 km and a medium flow rate of 8.7 $m^3 \cdot s^{-1}$ (highly variable between summer and winter) (source: SNIRH-APA). Another important watercourse in this site is the Grândola stream that like other small streams in the region is temporary, with a medium flow rate of 1.44 $m^3 \cdot s^{-1}$, ranging from 0 to 123 $m^3 \cdot s^{-1}$ among driest and wettest periods, respectively (source: STREAMES). This situation may cause the fragmentation of channel during summer into a series of isolated pools (Morais et al., 2004).

2.2. Geology and mineralization

The geological sequence at Caveira is represented from bottom to top by phyllites and quartzites (PQG), follow by a volcanic sedimentary complex sequence (VSC) unit (Late Famennian–Late Visean) represented by dark grey and siliceous shales and rare jaspers (Fig. 1). In the northern sector late intrusive diabase rocks are identified. The Caveira antiform contacts south-westward, by a major thrust, with the flysch Mértola Formation (Upper Visean).

The Caveira structure is controlled by N–S and NE–SW late-variscan faults and the polymetallic massive sulphide mineralization is located along a structural lineament of the VSC (Fig. 1), where the Volcanic Hosted Massive Sulphide (VHMS) type deposits are found (Oliveira et al., 2001).

The mineralization is distributed by several small massive sulphide orebodies: Salvador, António, Frederico, Pero-Cuco and Canal, with 22–65 m length dimension and 1.5–7 m thick. Two mineralised horizons are present in the western and eastern sectors of the Caveira N–S geological antiform structure, namely: Helena shaft sector hosting the Salvador–Esperança and NW–S João orebodies; and Luísa shaft sector hosting the Canal–Frederico–Francisco and Augusto–António orebodies (Castelo Branco, 1994; Matos et al., 2003a). Canal, António and Frederico orebodies are associated with black shales and felsic volcanic rocks (Matos, 2006) and located near de VSC/PQG (Late Strunian) contact (Fig. 1).

The mineralization of the Caveira is similar to that from Lousal (Matos and Oliveira, 2003; Strauss, 1970) and is dominated by pyrite (FeS_2), with variable amounts of chalcopyrite ($CuFeS_2$), galena (PbS) and sphalerite (ZnS). Other accessory minerals are pyrrhotite (FeS), marcasite (FeS_2), bournonite ($CuPbSbS_2$), tetrahedrite [$(Cu_2Ag_2FeZnHg)_3(SbAs)_2S_6$], arsenopyrite (FeAsS), cobaltite (CoAsS), goethite (FeOOH), magnetite (Fe_2O_4), and native gold (Au) (Matzke, 1971; Strauss, 1970). At the surface the sulphide mineralization is represented by narrow gossans and associated supergene kaolin alteration (Matos et al., 2003a), mainly in the western sector of the mine (Salvador orebody — Helena shaft). The gossans are represented by massive to banded hematite, locally with limonite and minor amounts of jarosite, hosting locally important grades of precious metals, namely Au (4.5 mg kg^{-1}) and Ag (45–300 mg kg^{-1}). The grade of Cu is <10% and S 3–6% (SIORMINP, 2002).

2.3. Mining activity and environmental issues

The Caveira mine has a long exploitation history that started in the Roman period. A large number of shafts, galleries and in situ tailings (>2 Mt — Matos et al., 2003a) are presented in the mining area (Fig. 1). The gossan and supergene zones of the two main horizons (Helena and Luísa shafts) were intensely mined between 1864 and 1886. The XIX century mine exploitation was conditioned by the site location (very isolated at that time) and by a great underground fire (1880 to 1882), related with pyrite spontaneous combustion (Matos and Martins, 2006). The mining activities took place until 1919, during the period between 1936 and 1943 and from 1952 to 1958.

The mining activity was responsible by significant downstream contamination (Cardoso Fonseca and Ferreira da Silva, 2000; Matos and Martins, 2006). The mine is characterized by the main tailing (approximately 2 Mt), two small acid water dams, several ruins of the