ASSINATURA GEOQUÍMICA DOS RESÍDUOS E PRODUTOS MINEIROS DE S. DOMINGOS, ALJUSTREL E NEVES CORVO NUMA PERSPECTIVA DE SUSTENTABILIDADE

FINGERPRINTS FOR MINING PRODUCTS AND WASTES OF THE S. DOMINGOS, ALJUSTREL AND NEVES CORVO MINES - A SUSTAINABLE PERSPECTIVE

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Resumo

O estudo que decorreu nas minas de S. Domingos, Aljustrel e Neves Corvo está integrado no projecto PROMINE - Nano-particle products from new mineral resources in Europe do 7 Programa Quadro da EU. No âmbito deste fizeram-se campanhas de geoquímica com vista à amostragem dos vários tipos de resíduos/produtos. Estudos anteriores forneceram critérios para a avaliação, numa perspectiva de sustentabilidade, de um dos três pilares: o ambiente, a economia e a realidade social. Em S. Domingos e Aljustrel obtiveram-se concentrações de elementos químicos de interesse, em diferentes tipos de resíduos. Em Neves Corvo depois de se analisar as amostras, compósitas mensais, do minério que entrou na lavaria da mina, do concentrado produzido e ainda do rejeito que foi para a barragem de Cerro do Lobo, foi possível observar concentrações interessantes de outros elementos, para além dos habituais produtos vendidos pela mina.

Palavras chave: sustentabilidade, S. Domingos, Aljustrel, Neves Corvo, resíduos mineiros

Abstract

The study conducted in the S. Domingos, Aljustrel and Neves Corvo mines is part of the research project PROMINE (Nano-particle products from new mineral resources in Europe), a EU 7th Framework’s Programme. Geochemical campaigns were conducted aiming the characterization of the mine’s wastes/products. Previous studies guided the evaluation, from a sustainable perspective, of the three main axes: environmental, social and economic. S. Domingos and Aljustrel mines showed high potential for wastes as new products Interesting concentrations of certain chemical elements were found. Concerning Neves Corvo mine we can say that, after the analysis of the mining plant ore, the correspondent concentrate and the rejected material, into the Cerro do Lobo dam, showed interesting concentrations for several chemical elements and not included in the mine trade.

Keywords: sustainability, S. Domingos, Aljustrel, Neves Corvo, mining waste
Introduction

Ore minerals reveal information on their origin and their life history. However, ore minerals are not just valuable as sources of metals to feed society’s demands but may also be viewed as environmental pollutants responsible for the generation of acid mine-waste runoff, for the increase of acidity to superficial waters, and for the release of various toxic metals into the environment. Or, on the other hand, after centuries of exploitation, this activity, like many others, shows the demands of ancient societies and in a historical perspective because mining has always been viewed as a major driving force in the development of civilizations (Craig, 2001). Successful mining of metallic ores requires great efficiency in metal recovery, which will require good understanding of ore textures, grade distribution and their implications with regard to mineral separation. Also, favourable market conditions and other factors such as accessibility, energy consumption and other production costs are key factors. These thoughts are important when looking for new products within previously exploited raw materials. At the same time, increasing awareness and concern over heavy metals in the environment will require better textural analysis of the pollutants in order to obtain environmental improvement with lower costs. Two mineral stages must be considered in mining waste: primary ores and secondary minerals formed after waste deposition. Furthermore, a balance between the products potential of a certain raw material with its heritage potential, if it is the case, or its environmental penalties, needs to be made. A first approach to the above mentioned issues but only related to the economic value of the wastes and the comparison between the different situations present in these three Iberian Pyrite Belt (IPB) Portuguese mines was the objective of this study.

Site characterization

The S. Domingos massive sulphide orebody, dominated by pyrite, is located at the top of a Volcano Sedimentary Complex (VSC) sequence represented by black shales, felsic, basic and intermediate volcanic rocks (Matos et al., 2006, 2010). The presence of chlorite, silica and sericite shows that they were hydrothermally altered. The massive sulfide orebody is bounded in the south by an intrusive diabase. In the northern side, the footwall hosts units that are represented by coherent rhyolites and rhyodacites, with columnar joints and basic volcanics.

Paleoweathering of the S. Domingos orebody has resulted in an important gossan horizon which was intensely mined during Roman occupation of the Iberian Peninsula and subsequently mined out in the XIX century.

In Sào Domingos the first products extracted, by incineration processes, were separated and the richest nodules were submitted to a fusion process. The leaching of the poor products was carried out in cementation tanks but this process was abandoned in 1868 because of their technical difficulties and high costs. When copper prices decreased, the mine management have decided to leach the material in a raw state, making the recovery more efficient (Cabral et al., 1889).

When the copper trade with England decreased, in the 1950’s, the S. Domingos mine increased the sulfur production for the Portuguese Companhia União Fabril (CUF) and subsequently used in the chemical industry and fertilizers.

The Aljustrel mining area is recognised as one of the greatest Iberian Pyrite Belt mining centres. The region is characterized by the presence of the NE–SW Messejana Fault which limits a southeastern block formed by the Iberian Pyrite Belt Palaeozoic basement (Schermerhorn et al., 1987; Matos et al., 2010) and a north-western block represented by de sedimentary overburden of the Sado Tertiary Basin. The Volcano Sedimentary Complex, in the Aljustrel area, is represented by siliceous shales, phyllites, tuffites, purple shales, jasper and cherts; felsic and metavolcanic rocks and megacryst, green metavolcanic sequences – sericitic felsic volcanics, felsites, felsophyres, volcanic breccias, feldspar megacryst volcanic lavas are host to six distinct ore bodies (Feitais, Moinho, S. João, Alarges, Estação and Gavião).

The Volcano Sedimentary Complex, Aljustrel Anticlinorium (Matos et al. 2010; Schermerhorn et al., 1987) is represented along a 4.5 Km NW–SE direction and a 1.5 km cross section. Close to the Messejana fault, in the São João area, the Palaeozoic structures are affected by the fault’s sinistral movement and present a NE–SW direction. Several NW–SE thrusts are identified, mainly in the short limbs of the anticlines. The Aljustrel thrust is one of the main structures and materializes the SW contact between the VSC and the Flysch Group.

Just as in S. Domingos, Aljustrel was also mined since pre-Roman times and was a very important Roman exploitation centre (Vípasca) is recognised on site. Modern mining began in the 19th Century. The 19th Century separation technology is described in Cabral et al. (1889) and carried out in “teleiras” a pyrite ore roasting process developed at Pedras Brancas, located 6 km east of Aljustrel. This process consisted of the reduction of ore fragments to 20-30 mm followed by a roasting process in layers of ore above layers of vegetation used as an energy source. The concentrates produced in this way were exported to England up to 1878.

In the 20th Century, between 1899 and 1988, 33 000t of Cu (70% rich) cement were produced, and between 1971 and 1990 1,439,000 t of ore
was used for the production of sulphuric acid at CUF facilities, located south of Lisbon.

Base metals were recovered by hydrometallurgical processes from the waste produced by the roasting process when producing sulfuric acid, zinc was recovered in the process. In 1991 the Moinho plant started producing discriminate Cu, Zn and Pb concentrates but the low prices of these metals forced the mine closure in 1993. Presently the Almina Company is working at Feitais and Moinho, developing a mining project focused in the copper concentrates production.

The Aljustrel mine is undertaking a rehabilitation process led by the Public Company EDM. In this process, mining waste from Pedras Brancas were transported to the main rehabilitation area, Algares.

Geologically, Neves Corvo is made up of three main groups of Devonian to Lower Carboniferous sequences: the Phylite Quartzite, the Volcano Sedimentary Complex and the Flysch Groups. The Volcano Sedimentary Complex is represented by a NW-SE antline with two main sequences, one autochthonous and the other, allochthonous. The base of the autochthonous sequence is composed of three units of schist with carbonate nodules interbedded with felsic volcanic rocks (Oliveira et al., 1997). Above these units lies the Neves Formation made up of black schists above which are hosted the orebodies. The allochthonous sequence is composed of siliceous schists and black pyritic and graphic schists at the base, grading upwards into green and purple (meta) shales, siliceous schists, tuffs and black pyritic schists. The sequence is topped by schists and greywackes (Oliveira et al., 1997).

Neves Corvo mine includes the five traditional orebodies (Graça, Corvo, Zambujal, Neves and Lombador) and has recently discovered another (Semblana). Previously, there were two plants: a copper plant and a copper-tin plant using conventional flotation and gravity methods for ore concentration (Real and Franco, 2006). Currently, there are also two plants but one for copper and the other for zinc. Both plants use conventional crushing, flotation, grinding, thickening and filtration processes. The copper plant capacity is of 2.2 Mt/year and the zinc plant capacity is 400,000 t/year. The copper plant achieved an average recovery of 88.4% and the zinc plant achieved an average of 81.3% recovery. After the primary underground crushing to 0.25 m the ore goes to the surface in a conveyor to a coarse ore stockpile to be blended to ensure a constant copper head and to keep the levels of penalty elements (e.g. As) below a predetermined limit.

**Materials and Methods**

These three IPB massive sulphide mines were used for this purpose because: 1- S. Domingos is a long abandoned mine, where economic perspectives could eventually be on the reuse and residues recycling; 2- the Aljustrel area is still a prospect where Cu, Zn and Bi exploitation as by-product is still in evaluation, Investments were made considering the reuse or waste recycling as a profitable hypothesis and 3- Neves Corvo is a totally different situation. It is a modern, highly productive mine where other interesting by-products (e.g. In and Se) could be evaluated as products.

Sampling of the mining waste of S. Domingos and Aljustrel were targeted, not representative of the whole waste pile. In places sampling was composite while in others sampling was made in profile. The Sào Domingos and Aljustrel mines have the most important and diverse volumes of wastes in Portugal (Matos et al., 2006, Abreu et al., 2010). In this study it was decided only to address two types of waste that may have had similar metallurgical treatment, (milled pyrite) and occupied considerable areas. This way, particular attention was given to the milled pyrite in the Achada do Gamo area in S. Domingos mine and milled pyrite in the Algares sector of the Aljustrel mine.

The sampling criteria were based on previously documented studies involving detailed geology, mine waste characterization and infrastructure mapping (Matos, 2004; Matos 2005 in: Abreu at al., 2010). Additionally, chemical and mineralogical characterization studies (e.g. Batista, 2000; Batista et al., 2003; Martins et al., 2007; Pinto et al., 2007; Álvarez-Valero et al., 2008; Luís et al., 2009; Silva et al., 2009; Abreu et al., 2010, Mateus et al., 2011) were used.

The Neves Corvo samples were provided by the mine plant management team and represent a monthly composite sample of the ore delivered to the Somi copper plant; the ore concentrate that leaves the copper plant and the rejected waste of this plant to the tailings pond of Cerro do Lobo.

Apart from the Neves Corvo samples that were provided already milled and ready for analysis, S. Domingos and Aljustrel samples were dried at 40ºC, crushed and milled. Samples for an exploratory analysis to a high range of elements were sent to ACTLABS in Canada to be analyzed by INAA for Au, As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, Ir, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Sn, Ta, Th, Tb, U, W and Yb. Also 4 acid extraction solutions measured by ICP for Ag, Al, Be, Bi, Ca, Cd, Cu, Ga, Ge, In, K, Li, Mg, Mn, Mo, Nb, Ni, P, Pb, S, Sr, Ti, V, Y, Zn and partial extraction expected for Zr. A small set of samples were also analyzed for platinum group elements (Os, Pd, Pt, Ru, Rh, Ir) and Re.

Many of these ore samples were reported with concentrations above an upper detection limit. Precise concentrations were not quantified but a semi-quantitative evaluation of those elements was undertaken using a Philips PW1400 automated X-ray fluorescence spectrometer.
equipped with a rhodium tube and a LiF200 analysing crystal. A rough idea of the intensity of the spectrum was obtained and by this method evaluated if there are high or medium concentrations.

The identification of the mineral phases was made with a Philips powder diffractometer with Bragg-Brentano geometry, equipped with a large-anode copper tube and a curved graphite crystal monochromator, was used to collect XRD spectra covering the angular 2θ region of interest for the identification of clay minerals, and a quartz reflection that used as reference to estimate the mineral content.

**Results**

Focus will be given to a profile in the S. Domingos sulphur factories area (Achada do Gamo) with milled pyrite ore (Fig. 1). The vertical profile was excavated in a 2 m high waste pile located 10 m east of the acid waters lagoon.

Vertical variation in colour occurs due to chemical alterations after the waste pile storage, and also as a result from differentiation related with the history of the deposition and development of the mining operations (Fig. 1).

The chemical characterization of the profile samples is represented in Table 1 where the profile presents in the seven sampled layers high concentrations of Au, Pb, Sn, Sb, Bi and Re. Volumes of similar materials need to be estimated at the S. Domingos mine but the unknown representative character of the samples needs to be taken into account (lateral and vertical mining waste zonation is difficult to improve without a detail exploration boreholes program). From the critical raw materials (Sb, Be, Co, CaF₂, Ge, Ga, Graphite (C), In, Mg, Nb, PGM, REE, Ta, W) the most interesting concentrations of the chemical elements detected were Sb and Ge up to 30 times the Crust abundance (1.5 mg kg⁻¹). But there are other valuable elements present in interesting concentrations some of which are: Re, Zn and Fe. Other interesting concentrations were obtained for Sn where all the profile concentrations are above 200 mg kg⁻¹ which is the upper detection limit. The relation along the profile between Sb and Sn is represented in the XRF diagrams in Fig. 2.

Table 1 – Re, Se, Sb distribution at in the profile of milled pyrite ore in Achada do Gamo, S. Domingos mine (mg kg⁻¹); Bi all profile above 2000 mg kg⁻¹ and Sn above 200 mg kg⁻¹

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Re</th>
<th>Sb</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP5 3-2</td>
<td>superficial</td>
<td>1.65</td>
<td>&gt;10,000</td>
<td>369</td>
</tr>
<tr>
<td>WP5 3-3</td>
<td>red layer</td>
<td>2.12</td>
<td>&gt;10,000</td>
<td>564</td>
</tr>
<tr>
<td>WP5 3-4</td>
<td>dark layer</td>
<td>3.06</td>
<td>5700</td>
<td>937</td>
</tr>
<tr>
<td>WP5 3-5</td>
<td>yellow layer</td>
<td>3.4</td>
<td>7780</td>
<td>738</td>
</tr>
<tr>
<td>WP5 3-6</td>
<td>grey layer</td>
<td>2.65</td>
<td>3560</td>
<td>507</td>
</tr>
<tr>
<td>WP5 3-7</td>
<td>basal layer</td>
<td>1.34</td>
<td>10,000</td>
<td>164</td>
</tr>
</tbody>
</table>

An increase in Sn with depth and a decrease in depth of Sb show the different behavior of the two elements in these conditions of weathering of the materials with time.

Table 2 – Mineralogical characterization of the materials in the profile of milled pyrite in Achada do Gamo, S. Domingos mine (mg kg⁻¹)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Identified phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP5 3-2</td>
<td>superficial</td>
<td>Ang + vtg H</td>
</tr>
<tr>
<td>WP5 3-3</td>
<td>red layer</td>
<td>Ang + vtg J</td>
</tr>
<tr>
<td>WP5 3-4</td>
<td>dark layer</td>
<td>Ang + vtg (Gy+J+Q)</td>
</tr>
<tr>
<td>WP5 3-5</td>
<td>yellow layer</td>
<td>Ang + vtg (Q+Anhydrite)</td>
</tr>
<tr>
<td>WP5 3-6</td>
<td>grey layer</td>
<td>Ang + vtg (J+Q+Anh)</td>
</tr>
<tr>
<td>WP5 3-7</td>
<td>basal layer</td>
<td>Ang + vtg (Anh+Q)</td>
</tr>
</tbody>
</table>

Mineralogical characterization of this profile can be observed in the table 2.
The minerals identified in the profile were: anglesite (PbSO₄), probably related to the alteration of galena, jarosite [(K,Pb)Fe₃(OH)₆[S,As]O₄]₂ indicating the weathering of iron sulfides, hematite (-Fe₂O₃), anhydrite (CaSO₄) usually associated to the sulfides and that can be altered to gypsum CaSO₄·2H₂O, also present in the profile. The identified mineral phases can act as traps for the metals, e.g. jarosite can incorporate Pb (Figueiredo et al., 2006).

In the Aljustrel mine the sampling of milled pyrite was made in Algares sector and the vertical profile is represented in Fig. 3.

The results presented are from the waste piles of milled pyrite ore which still have significant quantities of Au (280 µg kg⁻¹), Ag (mg kg⁻¹), Pb (above 5000 mg kg⁻¹), Sb (485 mg kg⁻¹), Sn (115 mg kg⁻¹) and Zn (887 mg kg⁻¹). Although high, these concentrations are lower than for the same type of waste in S. Domingos. This situation can induce different processes in the treatment where in Aljustrel (probable simple and coarse mill) the recovery of the metals was more efficient (Aljustrel mine was modern then S. Domingos), or just different types of primary ores (different mineral constitution of the São Domingos lens and the Aljustrel Moinho, Algares Aljustrel lenses) Information from the reports shows the difficulty in recovery of Zn in the treatment plant. Concentrations of Zn are not very low, but mobility of this base metal in the presence of acid mine drainage is higher (Abreu et al., 2010).

The sampling program carried out at the Neves Corvo mine had the objective to represent what is the present operational outputs of the copper plant from the ore being extracted presently in the mine (from Graça, Corvo, Neves, Zambujal oreebodies), especially concerning critical elements.

The results of Cu and S are above the upper limit of the method, but were not re-analyzed because other information provided by the mine indicates the real Cu concentrate and attention is given to the critical elements. Critical elements analyzed in the materials with significant concentrations are: Co, In, Mg and Sb from which Co and Sb are not concentrated with the Cu concentrate. Indium is concentrated along with the Cu, but 39% of the In present in the ore of entry still goes to the tailings. Other economically important chemical elements are: Fe, Zn and Al of which, Fe and Al are going to the tailings pound and Zn that is in 33% in the Cu concentrate about 0.8% still goes to the tailings, according to the results. Other interesting grades that still go to the tailings are Se and Sn.

Discussion and conclusions

In the mine life cycle re-mining operations can be considered related with the continuation of the underground and surface mining exploitation and/or reprocess of the old mining wastes, considering new extraction techniques, more specific and developed. In both scenarios it is important to know and understand the extent of available reserves, waste distribution and mineralogical/chemical content. Considering the complexity of the S. Domingos and Aljustrel mining areas, the presented data are limited to the vertical profiles of mining waste within the study areas. The Neves Corvo data is interesting considering the present mining operations and a probable future mining waste exploitation at the Cerro do Lobo waste dam facility. This study may contribute in the long run given that there are significant concentrations of other metals in the waste piles especially in the S. Domingos milled pyrite (Table 1), where the volumes are considerable (where volume in open pit milled pyrite is above 50000 m³). This volume pales in comparison to the situation at Neves Corvo where current mining keeps increasing the volume of waste piles. Furthermore, the milled pyrite in Aljustrel is an intermediate situation because it is an open mine but the grades in wastes are not so high and exploitation is still in a developing stage.

Further studies in Neves Corvo could determine a potential for exploiting by-products because these have appreciable concentrations of In, Mg, Co and Sb presently considered critical raw materials by the EU. Also, the comparison between the grades of some of the elements that enter in the copper plant and the ones that goes to the tailings ponds suggests that the recovery of these elements could be optimised, hence increasing the mine life. Present backfilling operations must be carefully considered as not to block access to ore sectors in the future. Further research should be developed in other locations of the considered mines.
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