



## METALS AND ARSENIC ENRICHMENT PROCESSES IN SULFIDE-RICH WASTE DUMPS – THE ROLE OF THE CLAY SIZE FRACTION

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## METALS AND ARSENIC ENRICHMENT PROCESSES IN SULFIDE-RICH WASTE DUMPS – THE ROLE OF CLAY SIZE FRACTION

### 1. Purpose

Abandoned mines pose some of the most outstanding environmental risks, namely related with potentially toxic metals and metalloids in mining soils. Mobilization or fixation of these elements in the soil particles can be regulated by the interactions between several biogeochemical and mineralogical processes. In this context, the present study is focused on the detection of metals and arsenic enrichment processes in different particle size fractions of two distinctive sulphide-rich waste dumps. Furthermore, the study evaluates the role of typical clay size minerals, such as oxyhydroxides and clay minerals in the retention of toxic elements.

### 2. Methodology

Two sulphide-rich waste dumps were selected in the N of Portugal: i) Mine of Santo António of Penedono, was an important gold mine, with gold occurring in quartz veins with sulphides, mainly pyrite and arsenopyrite; Cerdeirinha mine, was exploited for tungsten ores in a skarn deposit with sulphides, mainly pyrite and phryrrhotite. Both waste dumps have been formed by successive accumulation of fine wastes derived from hydrogravitic separation.

Soil samples were obtained from each site consisted of 4-5 composite samples by using a stainless steel auger with 17 cm higher. The pH and electrical conductivity (EC) were measured in a soil/water suspension of 1:2.5. Mineral compositions were determinate by X-ray diffraction (XRD) on a Philips X'pert Pro-MPD diffractometer, using Cu-K $\alpha$  radiation. The XRD diffractograms were obtained from powders (fraction <2 mm; fraction < 2  $\mu$ m fraction) and from oriented aggregates (<2  $\mu$ m fraction) in the interval 3 to 65°20 and 3 to 35°20 respectively. The finest fraction was obtained by the sedimentation method and the particle-size separation based on theoretical Stockes' Law. The clay mineralogy was determined using the oriented preparations, which were submitted to the following treatments: air-dried, ethylene glycol (EG)-solvated, and heated (490°C). Chemical analysis for metals and metalloids in both fractions was performed by inductively coupled plasma/mass spectrometry (ICP/MS).

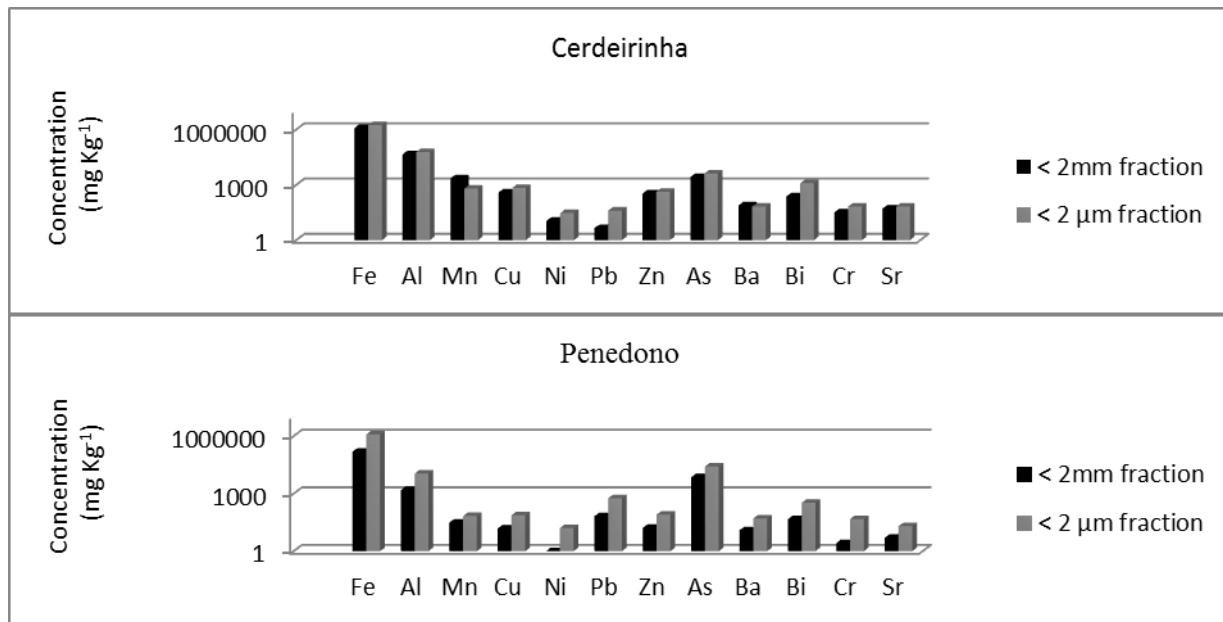
### 3. Results and Discussion

Soil physical properties and pH (< 4.5) were relatively similar in the two waste-dumps. According to the XRD analyses, the most common minerals in Cerdeirinha bulk soil are quartz, k-feldspar, plagioclase and mica. In a general, marcasite, phryrrhotite and pyrite are also prominent phases at this site. In contrast, Penedono shows lower mineralogical diversity, which is derived from the rather monotone inherited ore paragenesis. Important differences were identified in the <2  $\mu$ m: Cerdeirinha samples are dominated by the presence of iron oxyhydroxides (goethite), jarosite, gibbsite, mixed-layered mica-vermiculite and chlorite. In contrast, at Penedono, kaolinite and illite are the most abundant phases, followed by jarosite and smectite.

Metal and metalloid concentrations in the soil of the two waste-dumps are shown in figure 1. In both cases, geochemistry signature is marked by the dominance of Fe, Al, and As. Nevertheless, Fe and As occur in different ranges in the two sites, which can be justified by the differences in the inherited primary paragenesis. Cerdeirinha is dominated by iron sulfides, thus increasing the concentration of Fe. In Penedono, As mobilized from arsenopyrite is the most abundant element.



Moreover, at Penedono, all the elements appear with higher concentrations in  $<2 \mu\text{m}$  fraction, without exception. At Cerdeirinha, enrichment processes in the clay size fraction are mainly noticeable for Pb, As, and Bi. The magnitude of such enrichment can be expressed by the accumulation factor (AF), which was calculated by using the following equation:  $\text{AF}_x = X_{\text{fraction}} / X_{\text{bulk}}$ .



**Figure 1.** Concentrations of elements in different particle size fraction.

Cerdeirinha showed consistent values ~1.0 for Fe, Al, Cu, Zn, As and Sr. Some elements such as Ni, Bi, Cr and specially Pb showed higher AF. For example, AF for Pb reaches a value around 14. In contrast, Penedono reveals some differences. The AF values for this waste-dump are higher than 1 for all study elements, standing out Ni and Cr with 31.8 and 28.2, respectively. These strong enrichment in  $<2 \mu\text{m}$  fraction may be attributed to greater surface area per unit of mass of the fine particles, such as smectite, which increases the adsorption capacity of this fraction. These results suggest a higher capacity for retention of metals of the clay size fraction present in Penedono. Although, oxyhydroxides, such as goethite, are known by their high sorption capacity of trace elements, in Penedono goethite is vestigial. So, the mineralogical association composed by kaolinite, illite, smectite and jarosite seems more effective than the one present in Cerdeirinha. In addition to smectite, illite may also play a significant role in metals retention in Penedono. Isomorphous substitution of Fe in the octahedral sheet of illite, may justify that Ni and Cr tends to accumulate in the finest fraction. This may be an explanation for having a higher amount of these elements in the  $<2 \mu\text{m}$  fraction, especially in Penedono, where there is a significantly quantity of illite.

#### 4. Conclusions

The distribution of elements depends, in part, on the presence of sorption sites and mineralogical composition of soil. In a general way, the study of trace metals in two fractions demonstrated higher accumulation in the finer fraction, which is subject to greater dispersal of pollutants by wind, water and animals activity.