# Mineralogical composition and metals retention in the fine-fraction streambed sediments of an AMD affected system

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**Abstract** This work presents data from an abandoned mine (Valdarcas, NW Portugal) that, although submitted to environmental rehabilitation, stills presenting marks of AMD. Water and sediment samples from the riverine system were analyzed for chemical composition and mineralogy. Chemical contents of Fe, As and W in the < 20μm fraction indicate strong enrichment relatively to the water. Proportions of iron oxide-oxyhydroxides and clay minerals vary downstream, acting as mineralogical indicators of mining contamination. Additionally, the observed relation between the mineral proportions and metal concentrations indicates the relevance of each mineral phase to retain metals.

**Key Words** AMD, sediment, < 20μm fraction, oxide-oxyhydroxides, clay minerals, mineralogical control

## Introduction

Valdarcas mine is located in NW Portugal (fig. 1) and was exploited for W between 1950 and 1980. Ore paragenesis is diversified, including various generations of scheelite and wolframite, sulfides (pyrrhotite, pyrite, arsenopyrite), F-apatite, calcite and silicates. The relation between the complexity of ore paragenesis and the properties of acid mine drainage (AMD) was presented by Valente and Leal Gomes (2009).

The ore treatment included milling, hydrogravitic separation and flotation, from which resulted fine grained sulfide wastes. These processing wastes were accumulated without drainage control, promoting strong physical and chemical instability. Consequently, AMD affects the nearby aqueous system - Poço Negro creek (pH 2,8—3,4), and then the Coura river (fig. 1). As result of physical instability, the Poço Negro creek maintained a very high sediment load, mobilized from the waste-dumps. The hydrology of Coura river is affected by a dam for electric power production, located uspstream from the confluence of the AMD. Downstream (near C12, fig. 1) is located a public system for water supply (WPS).

During the years of 2007—2008, engineering rehabilitation works were conducted, comprising measures for erosion control and revegetation. Since then, the impact of this project has been subject to environmental monitoring, including the use of physical-chemical and mineralogical indicators. The main objective of the present work is to reveal the environmental quality of the riverine system, focused on the water-mineral interaction in the streambed sediments. Results show the mineralogical composition of the affected system, in what fine-fraction (<20μm) concerns. This fraction includes clay and silt particles that may exhibit aptitude for sorption. Therefore, chemical composition was analyzed, providing indication about the enrichment of the identified mineral phases in Fe, As and W and about the spatial dispersion of these metals along the riverine system.

## Methods

### *Sampling*

Sampling took place in September 2009, including sites along the main effluent channel (Poço Negro creek) (V3 to V7) and in Coura river (fig. 1). In this last, samples were collected upstream (C1), and downstream (C4 to C12) relatively to the confluence of the effluent. Therefore, C1 represents

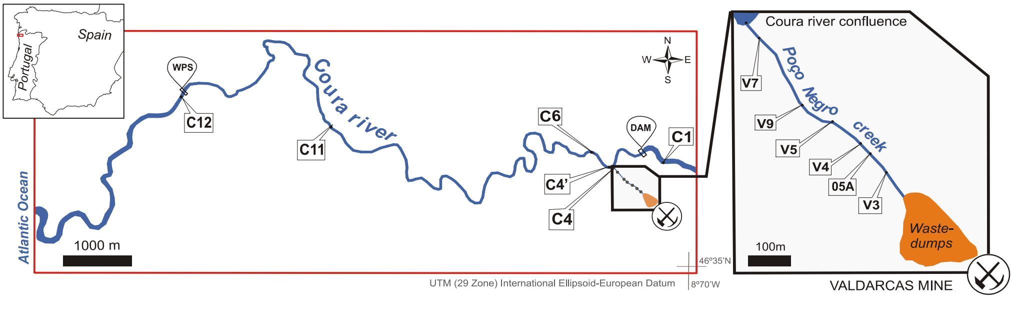


***Figure 1*** *Location of Valdarcas, with the sampling sites in the riverine system.*

the properties of the riverine system without the effect of AMD. At each site, water and sediment were collected and immediately transported to the laboratory in refrigerated conditions and protected from light.

### *Analytical methods for sediments*

The sediment samples were dried at 40ºC and sieved through a 2mm sieve. The <2mm size fraction was divided in two subsamples: one submitted to stereo microscope study of heavy minerals and UV identification of scheelite with estimation diagram and other was submitted to wet sieving with a 20µm sieve. This last was then analyzed for mineralogy and chemical composition. Mineralogical analyses were performed by X-ray diffraction (XRD) with a Philips PW1710 difractometer, using Cu Kα radiation at 40kV and 30mA. The difractometer is provided with automatic divergence slit and graphite monochromator. Powdered samples were measured at 0.02º2θ from 2 to 65º2θ, with a counting time of 1.25s. Semi-quantitative analysis by XRD was performed by using the peak-height intensities of the diagnostic reflections.

The powder material of the <20 µm size fraction was analyzed for Fe, As and W. For that, samples were submitted to an extraction with Aqua Regia and analyzed by inductively coupled plasma-mass spectrometry (ICP/MS) at Actlabs Laboratory (Canada).

### *Analytical methods for water*

Electric conductivity (EC), pH, redox potencial (Eh) and temperature of the water were measured in the field with a multi-parameter meter (Orion, model 5 Star). The following Orion probes were used: combined pH/ATC electrode Triode ref. 91—07, conductivity cell ref. 013010 and redox combination electrode ORP Triode ref. 91—79.

Laboratory analyses were preformed for sulfate and total acidity by turbidimetry and volumetric determination (Standard Methods for Water Analysis reference 4500E and 2310B), respectively. Inductively coupled plasma-optical emission spectrometry (ICP/OES) was used for metals, preceded by sample filtration through 0.45 µm pore-diameter cellulose ester membrane filters and acidification with $HNO_3$ 65% suprapur Merck.

## Results and discussion

### *Mineralogical composition*

The semi-quantitative phase content (tab.1) of the powder samples revealed that in the Poço Negro creek (fig. 1) there are quartz, plagioclase, mica (muscovite) and also the ore minerals (scheelite and wolframite). Clay minerals and gibbsite were detected in small amounts at upstream sites (V3 and 05A samples; fig. 2a).

Jarosite, schwertmannite and mainly goethite are present in different proportions along the creek. Goethite associated with schwertmannite or with jarosite (fig. 2b) are the characteristic mineral assemblages of V4, V5 and V7 samples.

Mineralogical composition of samples from Coura river presents a different pattern (tab.1). The mineral assemblages are dominated by the rock forming minerals, mainly quartz, with clay minerals and gibbsite occurring in almost all the sampling sites, although in small quantities (≤5% and ≤8%, respectively). Contrarily to the creek, in Coura river the iron oxide-oxyhydroxides are absent, with exception of goethite. This phase occurs in greater amounts in C4 (60%) and C4' (39%), which are immediately after the confluence of the mining effluent (fig.1). Additionally, the clay min-

***Table 1*** *Semi-quantitative mineralogical composition estimated by XRD of the bulk material in the <20µm size fraction. Q = quartz; F = K-feldspar; P= plagioclase; M= mica; CM= clay minerals; Gi= gibbsite; Go= goethite; Jt= jarosite; Sch= schwertmannite; W= wolframite; S= scheelite; Py= pyrite; tr=vestigial.*

| Samples | Mineralogical composition (%) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Q | F | P | M | CM | Gi | Go | Jt | Sch | W | S | Py |
| **V3** | 38 | - | 9 | 17 | 8 | - | tr | 10 | 12 | 6 | - | - |
| **05A** | 31 | - | 19 | 10 | 5 | 4 | 6 | 13 | 6 | 6 | tr | - |
| **V4** | - | - | - | - | - | - | 79 | - | 21 | - | - | - |
| **V5** | - | - | - | - | - | - | 62 | 38 | - | - | - | - |
| **V9** | - | - | - | - | tr | - | 34 | 40 | 26 | - | - | - |
| **V7** | - | - | 32 | 20 | - | - | 39 | 9 | - | - | - | - |
| **C1** | 54 | 14 | 8 | 12 | 5 | 7 | - | - | - | - | - | - |
| **C4** | - | - | - | - | - | - | 60 | - | - | 8 | - | 32 |
| **C4'** | 61 | - | - | tr | - | - | 39 | - | - | - | - | - |
| **C6** | 63 | 16 | tr | 10 | tr | 7 | tr | - | - | 4 | - | - |
| **C11** | 48 | 11 | 14 | 15 | 4 | 8 | tr | - | - | - | - | - |
| **C12** | 74 | 5 | 5 | 9 | 3 | 4 | tr | - | - | - | - | - |

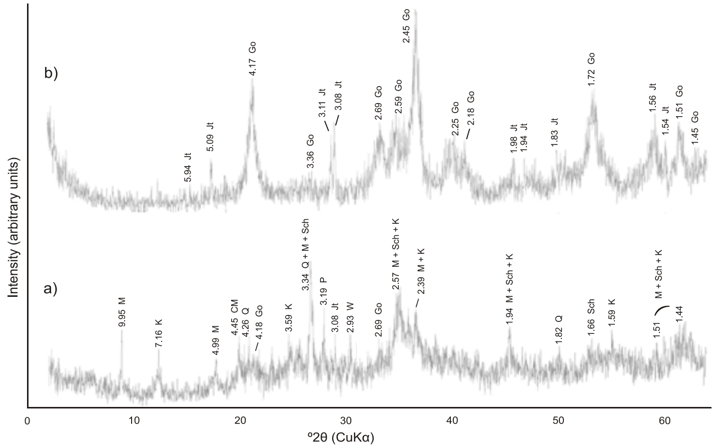


***Figure 2*** *XRD pattern of samples collected in the Poço Negro creek, showing d values in Å. a) V3 sample; b) V5 sample. K = Kaolinite; see other symbols in tab.1.*

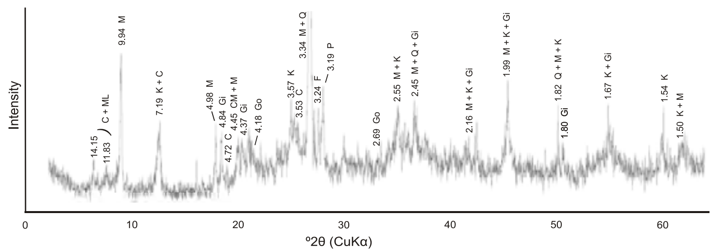


***Figure 3*** *XRD pattern of a sample collected at the Coura river (C12), showing d values in Å.; K = Kaolinite; C = Chlorite; ML = 10—14 Å Mixed-layer minerals; see other symbols in tab.1.*

erals are absent in these two more acidic sites. The presence of wolframite and pyrite in C4, C4' and C6 results from mechanical transport from the mining waste-dumps, upstream. This result is in agreement with the stereo microscope analyses of mineral concentrates from the stream sediment, which revealed abundant grains of heavy phases, particularly ore-minerals and sulfides.

This mineralogical behaviour indicates the presence of two distinctive geochemical environments as it will be shown below: i) the creek, with very acidic and sulfate conditions that allow precipitation of jarosite and schwertmannite (Bigham *et al.*, 1996) and ii) the Coura river, also affected by AMD, but with instability conditions for jarosite, due to dilution and other attenuation processes.

Regarding clay minerals, kaolinite is the dominant phase in the creek (fig.2a), while in the Coura river, besides kaolinite and chlorite, 10—14 Å mixed-layer minerals are also present (fig.3). As typically observed for iron-rich minerals formed in AMD, the identified clay minerals also present a very low degree of order (fig.2 and 3).

### *Chemical composition and partitioning*

Fig. 4 shows the spatial distribution of water parameters along the riverine system. Water samples collected at the Poço Negro creek present typical properties of AMD, with pH between 2.79 and 3.36 and high levels of acidity and sulfate. As the creek flows away from the waste-dumps is possible to observe an improvement in water quality. This is well noted at V7 (fig.5), which presents the lowest concentrations of Fe (21.5mg/L) and As (0.49µg/L) in the creek, suggesting the occurrence of mineralogical controls, namely by adsorption and precipitation. The results indicate retention of approximately 70% of Fe and 90% of As, between the upper section of the creek (05A) and its confluence (V7) (fig.1).

This spatial trend of improvement generally continues along the Coura river, until C12, near the public water supply system, where parameters have similar values to the non-affected river (C1). Concentrations of Fe and As increase in the confluence of the effluent in Coura river (between V7 and C4). This may be related with the dynamics of the riverine system in this sector. The irregular but frequent discharges of the dam located upstream (fig.1) creates hydrological instability and promotes desorption and remobilization of elements that may be transported as colloidal or particulate matter (Valente and Leal Gomes 2009)

Regarding chemical contents in the sediments, the results indicate strong enrichment relatively to the water. In order to describe the distribution of Fe and As between water and the iron-rich precipitates that are abundant in the Poço Negro creek, it was applied the concentration ratio (CR),

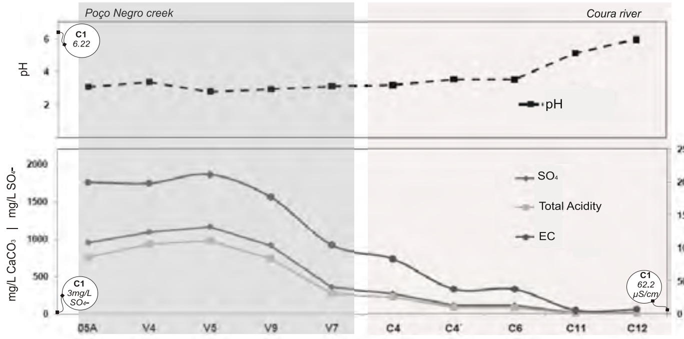


***Figure 4*** *Spatial variation of pH, EC, $SO_4^-$ and Total Acidity. C1 represents the non-affected system (fig.1).*

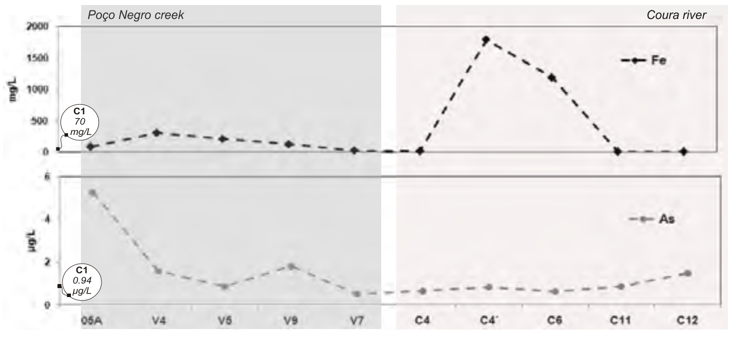


***Figure 5*** *Spatial variation of Fe and As in the water (see fig.1). C1 represents the non-affected system.*

defined by Munk *et al.* (2009) as $CR= (X)_s/(X)_l$; where $(X)_s$ is the concentration of an element in the precipitate and $(X)_l$ is the concentration of the element in the associated water. For Fe, the numerical values of log CR vary between 3.5 (05A) and 4.22 (V7), while for As it is between 5.41 (05A) and 6.22 (V5).

Fig. 6 shows the concentration of Fe, As and W in the sediment along the riverine system. The higher concentrations of Fe are observed in the samples that contain higher amounts of oxide-oxyhydroxides (V4, V5, V9 and C4'), indicating strong relation with the mineralogical environment (tab.1).

Arsenic presents similar behaviour, with higher concentrations at 05A and V5, where jarosite is abundant. Nevertheless, it should be noted the possible role of other phases in the retention of As, since high levels are also found in the samples with goethite, schwertmannite and clay minerals. These results are in agreement with the knowledge about the retention processes involving As and iron-rich minerals (e.g., Clayton *et al.* 2005, Hudson-Edwards *et al.* 2008, Valente *et al.*, 2011).

The sediment presents high concentrations of W, both in the creek and along the Coura river (fig.6). The higher levels are found in the upper section of the creek, particularly in sampling site 05A, which presents hydrogravitic and topographic conditions that act as gravity trap for the mining wastes transported from the waste-dumps.

The permanence of W in the sediments of Coura river, especially the high value analyzed at the most distant site (C12), suggests the occur-

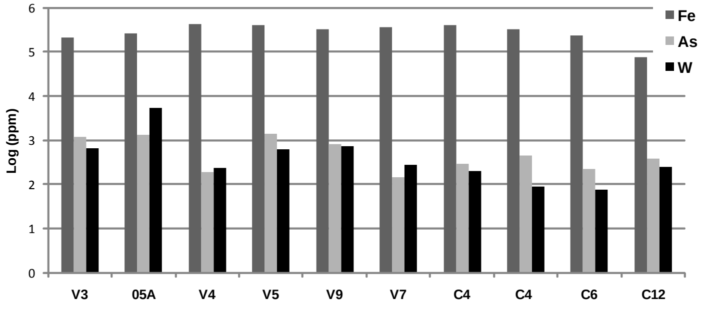


***Figure 6*** *Spatial variation of Fe, As and W concentration in the sediment along the riverine system.*

rence of gravity transport until near the river mouth. Mineral concentrates confirm the presence of scheelite, wolframite and sulfides. As a consequence of mining closing and decades of physical instability at waste-dumps, the riverine system has maintained a very high sediment load that justifies the presence of these mineral phases. Transport to long distances may be favoured by the hydrological instability promoted by the dam discharges. Drainage from other W mines in the region may also be contributing to the W increase that was observed between C6 and C12.

## Conclusions

The Valdarcas mine (NW Portugal) was abandoned for several decades, suffering strong physical and chemical instability. Although submitted to environmental rehabilitation in 2007, the results presented in this work show that water and sediment quality of the riverine system (Poço Negro creek and Coura river) stills affected by AMD and by the dispersion of sulfide wastes.

Analyses of water and sediment, combined with mineralogical study, revealed that mineral phases are enriched in Fe and As. They also suggest a trend of spatial dispersion of the heavy minerals (particularly ore W-minerals) to distances far from the waste-dumps. Two distinctive geochemical and mineralogical environments can be defined: i) Poço Negro creek, more affected by AMD, with equilibrium conditions for precipitation of jarosite, schwertmannite and goethite; clay minerals are rare and dominated by kaolinite; ii) Coura river, less acidic, which constrains the iron oxide-oxyhydroxide assemblage (only goethite); here clay minerals are dominated by kaolinite and mixed-layer minerals.

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## References

Bigham J, Schwertmann U, Traina S, Winland R, Wolf M (1996) Schwermannite and the chemical modeling of iron in acid sulfate waters. Geochimica et Cosmochimica Acta 60:2111—2121.

Clayton RE, Hudson-Edwards KA, Malinoovsky D, Andersson P (2005) Fe isotope fractionation during the precipitation of ferrihydrite and transformation of ferrihydrite to goethite. Mineralogical Magazine 69:667—676

Hudson-Edward KA, Houghton S, Taylor KG (2008) Efficiencies of As uptake from aqueous solution by a natural vivianite material at 4ºC. Mineralogical Magazine 72:429—431.

Munk LA, Faure G, Pride DP, Bigham JM (2002) Sorption of trace metals to an aluminum precipitate in a stream receiving acid rock-drainage; Snake River, Summit County, Colorado. Applied Geochemistry 17:421–430.

Valente TM, Leal Gomes C (2009) Ocurrence, properties and pollution potencial of environmental minerals in acid mini drainage. Science of the Total Environment 407:1135–1152.

Valente TM, Antunes M, Braga MA, Pamplona J (2011) Geochemistry and mineralogy of ochre-precipitates formed as waste products of passive mine water treatment. Geochemistry: Exploration, Environment, Analysis 11:103–106.