

# Acid Mine Drainage Precipitates at the Nanometric Scale – Properties and Environmental Role

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## Abstract

The mineral-water interactions responsible for mobilization of dissolved toxic elements in mine drainage often generate colloids that commonly occur at the nanometric scale. This study presents typical properties of these materials, mostly composed by iron-rich products. The samples were obtained in a variety of contexts, representing mine waters as well as natural acid rock drainage. It concludes by noting the potential influence of the waste and/or the host rocks on the hydrogeochemistry of the systems. Further, the water properties could control the morphology and mineralogy of this very fine material, and consequently its environmental role.

**Keywords:** Colloids, Nanoparticles, Iron-Rich Precipitates, Morphology, Arsenic

## Introduction

The mineral-water interaction processes that generate acid mine drainage (AMD) often contribute to the complete degradation of the ecosystems (Gomes *et al.*, 2020). In addition to the classical problems associated with the presence of dissolved potentially toxic elements (PTE), production of colloids (Wolkersdorfer *et al.*, 2020), especially in the most iron-rich waters, is a typical aspect in AMD. These colloidal particles, often denominated precipitates of mine drainage, ochre-precipitates or AMD-precipitates (Rait *et al.*, 2010), commonly occur at the nanometric scale (Waychunas *et al.*, 2005). They represent another important environmental concern as they may be responsible for mobilization of toxic pollutants to long distances from the mining sources. But these micro and nanoprecipitates may also form in neutral and alkaline conditions, affecting the behavior of PTE in the leachates, mining soils and the receiving surface and underground aquatic systems (Vriens *et al.*, 2020).

Characterization of these precipitates is a complex task due to aspects like heterogeneity, complexity of assemblages, and small dimensions of the nanoparticles. Therefore, insufficient knowledge about these complex natural mixtures could limit the applicability of first-principles of predictions. Thus, the present study aims to obtain mineralogical identification and detailed properties of nanoparticles resulting from the evolution of acid rock drainage (ARD) and mine waters, including neutral and acid mine drainage. Furthermore, geochemistry and morphology are discussed considering the potential ability to retain or promote the dispersion of contaminants, such as arsenic in the environment. Thus, the obtained results suggest that degree of crystallinity and surface properties associated with morphology may influence the resilience of the affected systems (water or soils) as these precipitates may contribute to the success of natural attenuation processes.



**Figure 1** Images of the sampling sites. *a* – Receiving stream of AMD from Valdearcas waste-dumps (NW Portugal); *b* – limestone channel in the passive treatment system of Jales mine (N Portugal); *c* – discharge of ARD from shallow groundwater in Serro (NW Portugal); *d* – discharge of AMD from Penedono waste-dumps (NE Portugal); *e* – stream affected by AMD in Campanario mine (Iberian Pyrite Belt, Spain); *f* – Receiving stream of AMD from São Domingos mine (Iberian Pyrite Belt, Portugal).

## Methods

Samples of ARD, mine waters, including AMD, and ochre-precipitates resulted from the evolution of these solutions were collected in different contexts. Fig. 1 shows images of the aquatic systems where sampling occurred. The sites were selected to cover a variety of paragenetic, climate, and environmental conditions. Another important idea was to represent sampling locations with a wide range of pH, in order to increase the possibility of distinguish different dominant types of nanoprecipitates. The location of sampling stations took in account the spatial heterogeneity of the AMD systems, defined from previous studies (Valente *et al.*, 2013; Prudêncio *et al.*, 2015; 2019; Valente and Pamplona, 2018; Gomes *et al.*, 2020).

Mine waters and ARD were characterized in the field for pH, electrical conductivity (EC), temperature, and redox potential with portable multiparametric equipment. Laboratory analysis was performed for sulfate by turbidimetry and acidity/alkalinity by volumetric titration. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for metals and arsenic in samples filtered ( $<0.45\ \mu\text{m}$ ) and acidified with  $\text{HNO}_3$  *suprapur* and immediately refrigerated in the field.

The precipitates were collected at the bottom of the streambeds and in artificial structures, like drainage tubes, and limestone channels in passive systems. Fig. 2 shows sampling procedures, such as directly scrapping the substrate and collection the suspended flocculated material. These fluffy



Figure 2 Sampling of precipitates in Acid Mine Drainage. a) Scrapping the substrate and b) slight agitation of the water for obtaining the flocculated material (fluffy precipitates).

**Table 1** Properties of mine in consulted at Valente *et al* (2013)\*; Gomes *et al* (2020)\*\*; Valente *et al* (2019)\*, and Valente and Pamplona (2018)\*\*.

Site	pH	CE	SO <sub>4</sub>	Ac	Alk	As	Fe (mg/L)
Valdarcas (n = 12) V4*	3.15	1664	974	752	-	0.993	178
São Domingos (n = 4) P6**	3.33	1568	687	265	-	0.010	8.16
Campanario (n = 4)	2.74	3245	2320	1138	-	0.168	372
Reboleiro*	6.10	315	2.45	-	nd	64.8	180000
Serro**	3.80	433	179	152	-	0.150	0.140
Jales (n = 4)	6.55	484	42.4	-	146	34.6	143

precipitates were concentrated by centrifugation at 4000 rpm. The other samples were sieved with a 20 µm stainless sieve and washed with MilliQ water. They were dried at room temperature and analyzed by X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM/TEM), and Fourier-transform infrared spectroscopy (FTIR).

## Results and discussion

### Mine waters and ARD properties

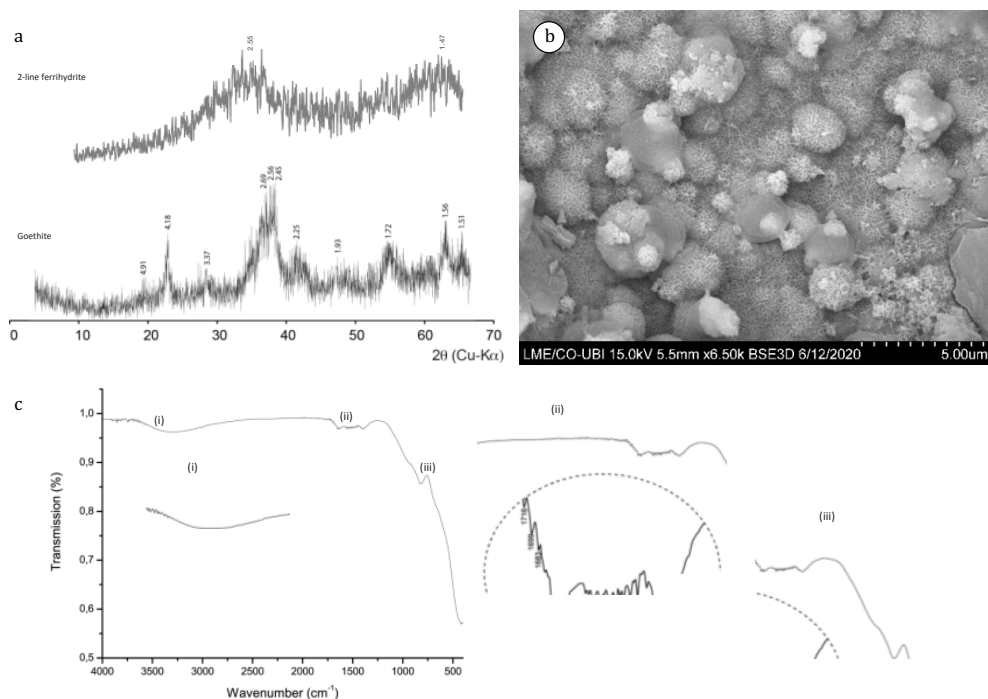
Table 1 shows the main properties of several waters from which nanoprecipitates are formed. They are in the range of pH of 2.74–6.55. The samples from Jales (Au-mine with arsenopyrite in quartz veins) were collected at the end of a limestone channel. Therefore the results reflect neutralization process, revealing alkalinity and high concentration of arsenic in agreement with the ore paragenesis. Reboleiro is mine water collected at the exit of a gallery of an abandoned U-mine. It was not submitted to any treatment, so the near neutral pH is a natural property. Serro is natural acidic shallow groundwater, as the sampled well was built in a sulfide-rich media, representing a case of ARD. All the other samples show typical features of AMD. Valdarcas has a special paragenesis, in which the sulfides coexist with calcite and chalcosilicate minerals from a skarn deposit (Valente *et al.* 2013). Therefore, the effluent should reveal this antagonistic chemistry of the wastes. However it was not enough to assure neutralization. Furthermore, even with addition of limestone along the creek

after closure, the creek maintains pH and concentrations of acidity and sulfate in the range of AMD. São Domingos and Campanario are both in the Iberian Pyrite Belt (SW Europe). The low pH and high concentrations of sulfate and acidity are compatible with the abundance of massive sulfides and absence of minerals with neutralization ability.

### Nanoprecipitates

The results indicate that precipitates from a variety of sites are oxyhydroxides and hydroxysulfates, mostly with low crystallinity or even amorphous (Fig. 3). XRD revealed the presence of ferrihydrite as the lowest crystalline phase, with two weak and broad bands at 2.56 and 1.47 Å, corresponding to the 11 and 30 *hk* reflections of 2-line ferrihydrite. The combination of methods – XRD, SEM, FTIR and TEM allowed confirming identifications and observing morphological features (Fig. 3).

Goethite, schwertmannite and jarosite were identified in the sites with typical AMD hydrochemical characteristics as already referred by other authors (e.g., Stoffregen *et al.*, 2000). For example, at Valdarcas and Campanario the ochre precipitates are often mixtures of these three minerals, but with dominance of schwertmannite. On the contrary, schwertmannite is rare at São Domingos, where jarosite is the dominant phase. Weakly crystalline goethite was the only ochre-precipitate identified in ARD, also in accordance with the pH <4 (Bigham *et al.*, 1996).



**Figure 3** Examples of identified phases in the ochre precipitates *a* - XRD analyses revealing patterns of weakly crystalline goethite in ARD of Serro and ferrihydrite in Jales; *b* - typical pin-cushion morphology of schwertmannite in a sample from Campanario (SEM image); *c* - FTIR, showing the typical bands of ferrihydrite (Fh) in Jales.

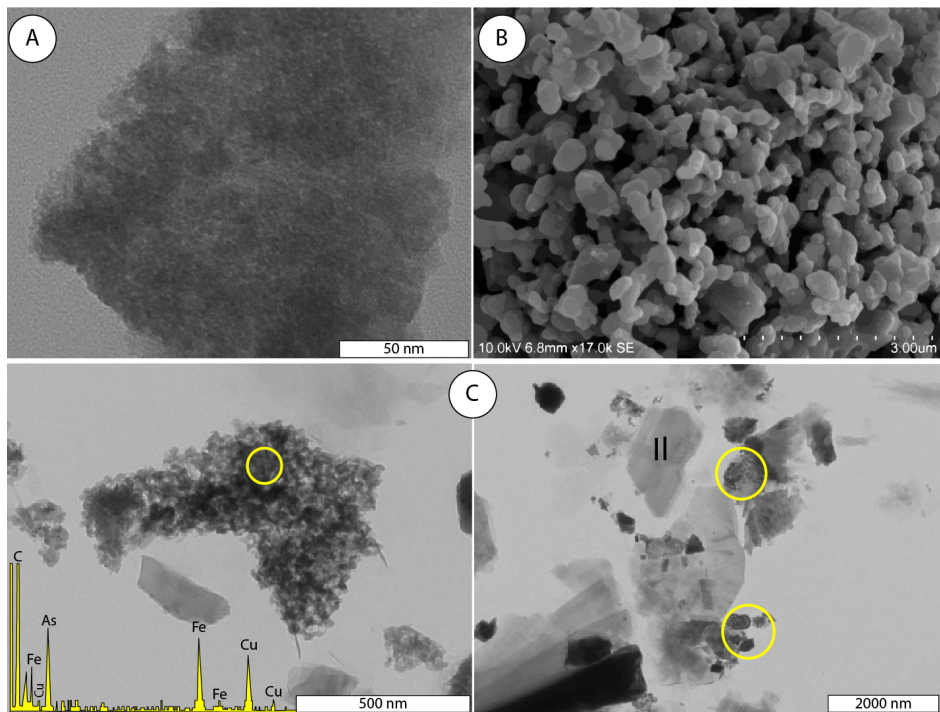
The typical globular aggregates observed in SEM and TEM as well as the analyses of the FTIR spectra (Fig. 3c) confirm the occurrence of ferrihydrite only at Jales and Reboleiro. This result suggests the control of hydrochemistry, and special of the pH, over the mineralogy of the precipitates. In accordance with Bigham *et al.* (1996) ferrihydrite was identified in the sites with higher pH, in the range of 6-7 (Tab. 1). FTIR patterns allowed or confirmed identifications of low crystalline and amorphous compounds, showing the co-existence of different iron-rich minerals in the nanoprecipitates (Gadsen, 1975). The vibration bands centered at 420 and 819 cm<sup>-1</sup> suggest the presence of arsenic-rich compound (Rout *et al.*, 2012), indicating the role of ferrihydrite in retaining As.

Less crystalline or even amorphous compounds were identified by TEM in Penedono samples (Fig. 4). As already referred by

Valente *et al.* (2015), iron and arsenic-rich nanoprecipitates appear with spherical shapes, often associated with jarosite and clay minerals. Therefore, these nanoparticles are also fixing the arsenic in the waste dumps, and so limiting the mobilization of this toxic element to the aquatic environment.

## Conclusion

Schwertmannite, ferrihydrite, and goethite were the most common identified low-crystallinity minerals. Different morphologies were observed, but there is a predominance of spherical and tubular aspects. The occurrence of these phases, pure or as complex mixtures, depend mainly on the hydrochemistry conditions. FTIR and TEM put in evidence the occurrence of the most weakly and amorphous crystalline phases. Their composition indicates ability to retain arsenic.



**Figure 4** Images of ochre precipitates A, B – TEM and SEM micrographs of a 2-line ferrihydrite; C – TEM micrographs and EDS spectrum of iron and arsenic-rich nanoprecipitates, showing globular and spherical morphology (marked in yellow) associated with clay minerals; II - Illite.

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