Mobility Control Of Uranium And Other Potentially Toxic Elements In Mine Waters By Ochre-Precipitates

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Abstract

Mineral-water interaction in mine drainage often results in the formation of iron-rich precipitates, called ochre products. They often comprise particles in the nanoscale, known by their strong reactivity. The present study focuses on these nanoprecipitates formed in streams that receive water from a U-Ra mine. Water and the ochre-precipitates that cover the streambed were sampled for geochemical and mineralogical characterization. Results indicate low crystallinity and variety of morphology of the ochre product, which is mainly composed by ferrihydrite in coexistence with minor hematite. The work concludes by noting the potential relevance of these nanophases in fate and transport of elements that pose major environmental concern, namely in uranium-rich mine waters.

Keywords: Uranium-mine waters, ochre-products, ferrihydrite, nanoparticles

Introduction

Degradation of water quality by mining activity is a typical environmental problem worldwide. Although acid mine drainage (AMD) is the typical effect associated with metallic exploitations due to mobility of metals and arsenic at low pH, circumneutral mine waters may also affect ecosystems. Potentially toxic elements (PTE) may occur in high concentrations in neutral and alkaline waters as documented by several authors (e.g, Lottermoser 2010). As referred by Lindsay et al. (2015), conditions of circumneutral pH favors mobility of PTE, like As, Se and U in the form of (hydr) oxyanions that may be responsible for contamination of the streams that receive mine discharges. Moreover, development of other typical indicators of mine water effect, such as deposition of ochre products, occurs in such water systems. These ochre-precipitates have been documented in other mining sites as strongly reactive due to small grain size and high specific surface area (Valente et al. 2012). They have dual and opposing effects. On one side they may disturb aquatic organisms and induce toxicity (Seo and Kwo, 2010) but on the other hand they may act as sinks for PTE.

The present work focuses on this last aspect, studying the result of mineral-water interaction in circumneutral mine water from a U-Ra mine. Therefore, hydrogeochemical and mineralogical studies were performed in a small stream that receives water from a mine located in the Argozelo area (Ribª Boco mine, Guarda, Central Portugal). The ore deposit is mainly of supergenic nature with dominant mineralization in authonite and torbernite. The regional geology is characterized by smoky and zoned quartz veins and basic rocks with pitchblende, sulphides, and secondary uranium minerals (Cameron 1982). Underground exploitation resulted in waste rock dumps with high concentration of radionuclides. High levels of radiation have been reported in the surrounding water and soil (Carvalho et al., 2014).

Surface runoff and mine water are discharged into a small creek (Boco creek), which displays typical features of mine contamination, such as deposition of yellow-reddish precipitates (Figure 1). Characterization of these products is a complex task due to small dimensions and, generally, low crystallinity of the phases (Valente et al., 2016). Therefore, the present work intends to (i) obtain mineralogical identification, morphology, and chemistry of the ochre-precipitates; (ii) elucidate about the nanoscale properties and ability to retain and constrain mobility of uranium, thorium, and other potentially toxic elements (PTE).

Methods

The mine is included in the Uraniferous Region of the Beiras-Central Portugal (Cotelo Neiva, 2003). It was selected as representative of other small U-Ra mines, with similar paragenesis and that generate neutral and reduced iron-rich effluents. Samples of ochre-precipitates were collected in a small pond formed by the accumulation of water discharged through the gallery. Six water samples were also collected, spatially distributed along ≈ 500 m of the small stream that receive this mine water (Boco creek). The first sample was obtained in the same site of the ochre-precipitates (at the exit of the gallery).

Temperature, pH, Eh, and electrical conductivity (EC) were measured *in situ* using a muliparameter HANNA HI929828 model. The water samples were filtered through 0.45 µm pore size membrane filters. Those for the determinations of major and trace elements (e.g. Ca, Mg, Fe, U, Th, As, Co, Cd, Pb, Cu, Zn, and Mn) were acidified with *suprapur* HNO_3 at pH 2 and analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), using a Horiba Jovin Yvon JV2000 2 spectrometer. Anions were determined in non-acidified samples by ion chromatography with a Dionex ICS 3000 Model. Duplicate blanks and laboratory water standards were analysed for quality control.

At the same site, ochre-precipitates were collected and stored in polyethylene containers protected from light until transport to the laboratory. The ochre samples were wet-sieved to obtain the fraction < 20 µm, using ultrapure water (Milli-Q) in order to remove impurities, and then dried at 40°C. Colour was analysed in dry samples by using Munsell system. The mineralogy was obtained by X-ray powder diffraction (XRD) using CuKα radiation at 40 kV and 30 mA. The ochre-precipitates were also submitted to heating at temperatures between 350 and 950°C following the procedure described in Brindley and Brown (1980) and applied by Valente et al. (2012). The morphology of the particles was studied by field emission scanning electron microscopy (FESEM), using a FESEM Jeol JSM-7001F microscope, equipped with an Oxford EDS light element detector at an acceleration voltage of 15 kV, after coated with chromium film. The chemical elements analysed in water were also determined in the ochre-precipitates by ICP-OES after digestion with *aqua regia*.

Blanks, replicates and stock solutions were used to assess quality control of the results. The accuracy of the methods was verified using certified patterns and the measurement

Figure 1 Field images of ochre-precipitates in the mine water receiving creek. a) Pond at the exit of the gallery; b) Boco creek, ≈ 500 m downstream the gallery

precision was greater than 5% RSD. The chemical composition of water and ochre-precipitates represents an average of three replicate determinations. Metals and arsenic were analysed in the "Department of Earth Sciences, University of Coimbra, Portugal."

Results and discussion

Water chemistry

Table 1 shows the properties of the water at the exit of the gallery and at the receiving creek. The first is circumneutral and reduced mine water with high concentration of Fe (18%). This high content of Fe is in accordance with the reducing nature of the source gallery (-61 mV). In general, the water creek reflects a decreasing trend relatively to the mine water, which is very clear for some elements, like Fe. The Eh values increase considerably (-61 to 125 mV), which can be associated with oxidation and hydrolysis of iron. As a consequence there is a strong decline in iron concentrations, associated with the precipitation of the ochre-products that are highly abundant immediately at the exit of the gallery.

Ochre-precipitates

XRD analysis reveals the low crystallinity of the ochre-precipitates (Figure 2-a). The XRD pattern allows identification of ferrihydrite, with the two weak and broad bands, at 2.56 and 1.47 Å, with the stronger band for the 11 and 30 hk reflections of 2-line ferrihydrite (Schwertmann and Cornell 2000, Schwertmann et al. 2004). Colour reference in the Munsell system (air dry conditions) was light brown, 5YR 5/6, which is in the range indicated for ferrihydrite (Dixon et al. 1977).

The thermal treatments are often used to understand transformation induced by dehydration on the iron phases. The sequence of XRD patterns in figure 2a-b shows such transformation. Ferrihydrite transforms in a poorly crystalline hematite at 350°C, which,

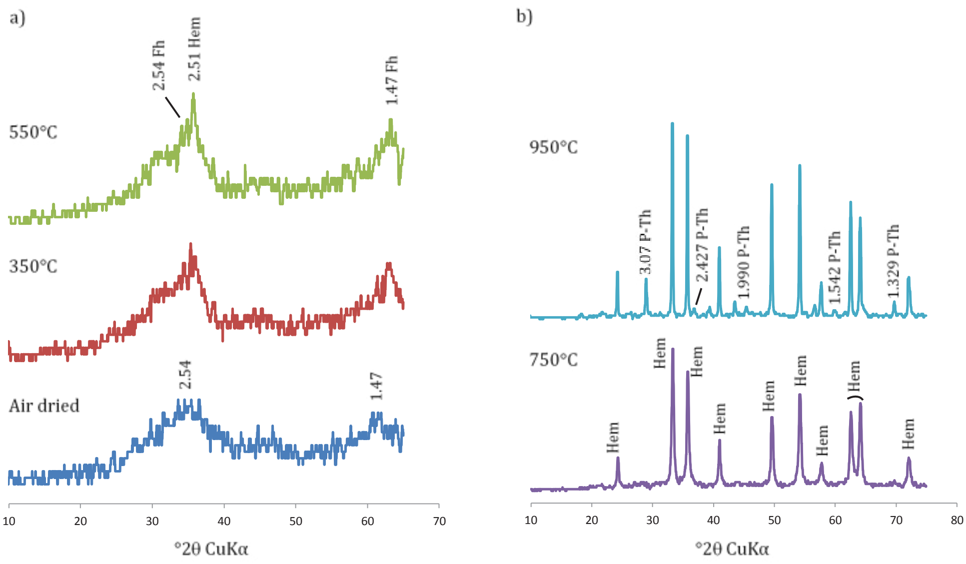

Figure 2 *XRD patterns of ochre precipitates. a) Sequence of transformation until 550°C. b) Crystalline hematite (750°C) and Th-phase (750-950°C)*

Table 1 *Water properties of the mine water (at the exit of the gallery) and downstream at the creek.*

Sample site	pH	EC (µS/cm)	Eh (mV)	Fe (%)	Cu	Zn	Cd (µg/L)	Pb	As	U	Th
Gallery	6.1	315	-61	18	10.46	22.75	79.23	17.43	64.77	43.99	19.66
Creek (n=6)	6.5	60	125	0.05	12.19	36.17	18.19	18.81	49.75	17.00	17.55

as expected, is finally perfectly crystalline at 950°C. Moreover, as observed by Valente et al. (2012), heating may lead to the formation of other compounds evolving due to specific elements that are adsorbed on the surface of the natural ochre-precipitate. In the present case, in coexistence with hematite at 950°C, the assay leads to the appearance of reflections compatible with the XRD pattern of a P and Th phase, specifically thorium nitride phosphide (PDF file 24-1321). This result is in accordance with the identification of the phosphorus element in the EDS spectrum obtained by FESEM (Fig. 3-a). Therefore, the EDS analysis confirms a composition compatible with an iron oxyhydroxide with minor amounts of phosphorus.

The images in figure 3 illustrate morphological aspects that suggest some structural order of the very small grained phases (<100 nm). There are globular aggregates, typical of ferrihydrite (Figure 3-a), but also filamentous and tubular structures, like hollow tubes with iron particles on their surface, as shown in Figures 3b-c. These tubular structures were previously documented for biogenic iron-rich precipitates (Peng et al., 2013, Ishihara et al., 2014), including schwertmannite in AMD (Valente and Leal Gomes, 2007). Figure 3-d shows also the presence of spherical nano-particles. Therefore, though XRD study indicates only the presence of natural ferrihydrite, FESEM images expose varied shapes, including the typical spherical morphology of hematite.

As stated by Fisher and Schwertmann (1975) nucleation of hematite from ferrihydrite is favored over goethite at neutral pH, which justifies the absence of this phase in the ochre precipitates. Thus, ferrihydrite in the ochres may represent different aging stages, and hematite could develop at expenses of the ferrihydrite aggregates.

Enrichment process

Table 2 presents the chemistry of the ochre-precipitates, indicating the dominance of

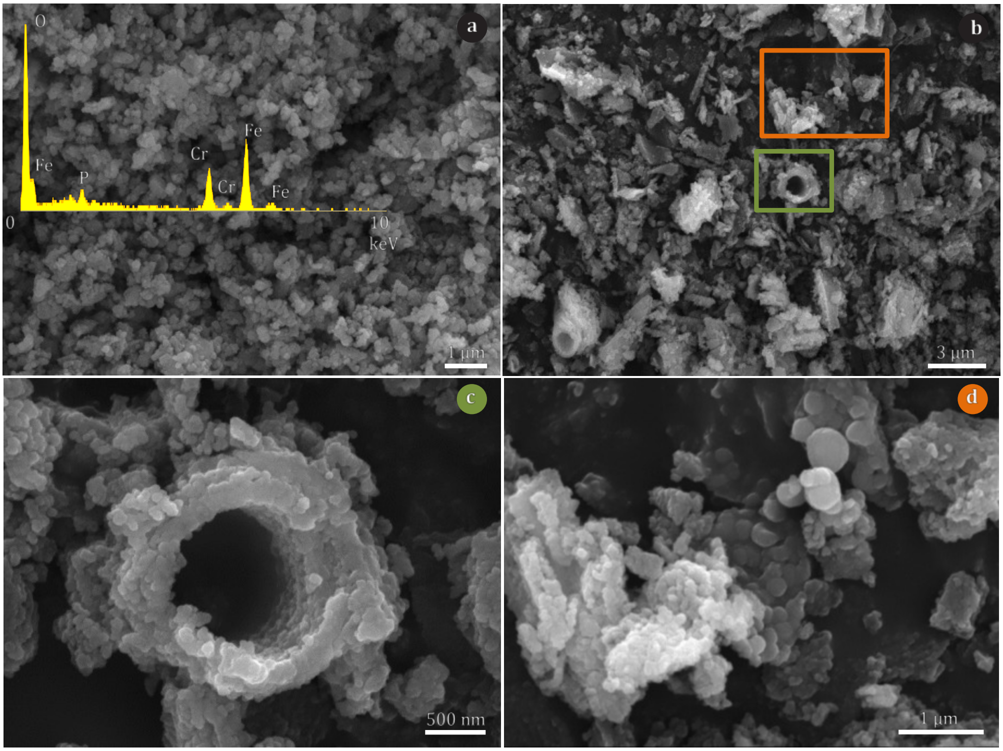

***Figure 3** Morphology of ochre-precipitates. a) Globular aggregates typical of ferrihydrite and the EDS spectrum. b) General view of different morphologies. c) Detail of tubular structures marked in b). d) Detail of an area with spherical and globular morphology.*

iron, in accordance with the presence of the iron-rich phases indicated by XRD and FESEM. The ratio between the dissolved elemens and Fe in both water and ochre is also shown in table 2. Combining data in table 2 with the water chemistry (Table 1) it is possible to infer about the role of the ochre-precipitates in retaining PTE. An enrichment factor (EF) was also calculated through the relation between the concentrations in the solid and in the water (Munk et al. 2002). The EF, represented in Figure 4, shows that some dissolved elements, like U, may have strong affinity to the ochre-precipitates, occurring with concentrations up to tens of thousands orders of magnitude. High EF was also detected for Th and Pb (≈7000). This affinity is in accordance with the ratios presented in table 2. Such results suggest the scavenging/sorption of PTE by the ochre. Also, co-precipitation of PTE like As and Cd along with iron may be occurring as a result of changes in redox conditions.

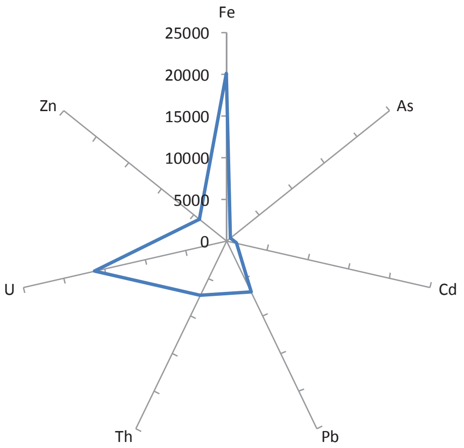

***Figure 4** Enrichment factor (EF) of PTE on the ochre-precipitates (EF = [ochre]/ [water])*

Conclusion

Ochre-precipitates from a U-Ra mine water are mainly composed by nanoparticles of ferrihydrite as revealed by XRD and FESEM. The analyses indicated a variety of morphologies, including tubular structures typical of biogenic iron products. Moreover, the study showed the coexistence of hematite, probably formed from evolution of ferrihydrite. In addition to Fe, other elements present in the mine water are enriched in the ochre-precipitates. Some of them show affinity to the ochre, as indicated by the high values of EF. Furthermore, the development of a crystalline Th, P-host phase, through heating experiments, suggests the possible adsorption/co-precipitation of these elements on the surface of the ochre-precipitates. In conclusion, the mixture composed of nanoparticles of ferrihydrite and hematite acts as sink of U and Th, as well as other PTE, like Pb and Zn, controlling their mobility in the mine water affected-system.

Acknowledgements

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***Table 2** Concentration of Fe (%) and PTE (mg/kg) in the ochre, and ratio (%) between PTE and Fe*

	Fe	As	Cd	Pb	Zn	Th	U
Concentration	38	37.52	95.03	118.4	95.49	142.37	713.8
ratio (water)	-	0.346	0.423	0.093	0.121	0.105	0.235
ratio (ochre)	-	0.009	0.025	0.031	0.025	0.037	0.199

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