

Anaerobic reduction of adsorbed X-Ferrihydrite (X = 0, AsO₄ and MoO₄) at pH 8 and 10

MARIO A. GOMEZ^{1*}, AND JIM HENDRY³

¹University of Saskatchewan, Department of Geological Science, Saskatoon, Canada, mag346@mail.usask.ca (* presenting author) and jim.hendry@usask.ca

Introduction

Uranium ore tailings produced in northern Saskatchewan, Canada often contain elevated concentrations of **As, Se, Mo and Ni**, (elements of concern, EOC). These EOCs are immobilized within the tailings solid phase through complexation (chemical adsorption) or co-precipitation with ferric oxide (HFO) minerals such as ferrihydrite (FH).[1-2] Although the redox conditions in the tailings are oxidic, even after 15 years of storage, concern exists as to impact of the development of anaerobic conditions at depth ($E_h \sim 500$ mV) on the stability of these EOCs. Research suggests HFOs are unstable under moderately reducing conditions ($E_h \sim +100$ mV). As a result, they may undergo phase transformation and redox active species (such as Fe, As, and Se) may undergo reduction of their oxidation states. To understand the impact of an anoxic environment on the stability of the EOCs, a set of anaerobic reduction test were conducted on pure synthetic adsorbed systems and on more complex tailings samples.[2]

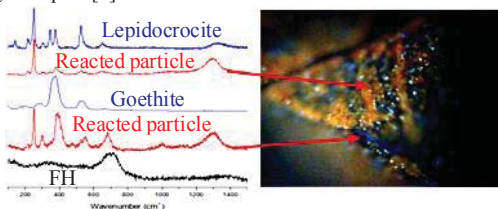


Figure 1: Micro-Raman and optical image of reduced X-FH particle

Results and Conclusion

We investigated solids with X/Fe molar ratios of 0, ~4, ~30 (X= 0, As and Mo) which are similar to those found in the DTMF products [1,2] and reacted these under two sets of conditions for all our products: high and low $[Fe^{+2}]$ at pH 8 and 10, using lime as a base (as per the industrial process). In the case of the pure FH @ pH 8 and 10, phase transformation to lepidocrocite-goethite and complete uptake of the Fe^{+2} added were observed (Figure 1). For the AsO₄-FH samples, only samples at higher Fe/As ratios (~4) was phase transformation not observed (via Micro-Raman nor PXRD) at both pH's irrespective of the $[Fe^{+2}]$. Significant arsenic release (~10 ppm) was observed in the case of Fe/As 4 and pH 10. In case of the MoO₄-FH, phase transformation to goethite-lepidocrocite was observed at all Fe/Mo ratio's at pH 8 but not at pH 10. High Mo release (> 20ppm) was observed for the Fe/Mo ~4 solid at pH 8, and pH 10 for both Fe/Mo solid ratios. The difference in chemical properties such as phase transformation and element release of these molecules may be attributed to their X-O bond lengths (As-O= 1.68 Å vs. Mo-O= 1.76 Å), and chelating nature (inner vs. outer sphere) in the adsorbed state to FH.[1,3]

[1] Moldovan *et al.* (2003) *Environ. Sci. Tech* **37**, 873-879.

[2] Shaw *et al.* (2011) *Appl. Geochem.* **26**, 2044-2056. [3] Brinza L. (2010) *PhD Dissertation thesis*, University of Leeds.

Enhanced metal release from acid mine drainage sediments due to the interaction with municipal waste water

MÁRIO A. GONÇALVES^{1,2*}, JOÃO C. WAERENBORGH³, FLÁVIA MAIA⁴, CLÁUDIA PINTO¹, CÁTIA PRAZERES⁵ AND SUSANA SÉRIO⁶

¹Department of Geology, FCUL, Lisbon, Portugal, mgoncalves@fc.ul.pt (* presenting author)

²CREMINER/LARSys, University of Lisbon, Lisbon, Portugal

³Instituto Tecnológico e Nuclear/CFMC-UL, Dept. of Chemistry, Lisbon, Portugal, jcarlos@itn.pt

⁴AMPHOS21 Consulting SL, Barcelona, Spain

⁵Laboratório Nacional de Energia e Geologia, Alfragide, Portugal

⁶CEFITEC, Department of Physics, FCT-UNL, Monte da Caparica; Portugal

The mining area of Aljustrel belongs to the well-known Iberian Pyrite Belt in Portugal. In spite of recent reclamation of the land where the old tailings were deposited, there is still a significant production of acid drainage waters that flow to the north in the Ribeira da Água Forte watershed. The stream waters are mixed with municipal waste water at 2 km from the source, for reasons that ultimately reside on the potential attenuation capacity of this high pH, low E_h , and organic-rich water. Although the visual impacts on the landscape seem to be attenuated, this apparently idyllic situation hides an unsuspected increase of metals in the flowing waters all along the stream length. This situation was detected because during large periods of the year in the dry season, the flow along the stream is mostly fed by the waste water with little or no input from the acid drainage waters. However, the stream hydrochemistry reveals that not only all the important trace metals remain equally concentrated in solution, but also that the stream waters are a bit more acidified as compared to the situation when mixing with the acid drainage waters from the old tailings occurs.

A detailed study of the stream sediments mineralogy by XRD and Mössbauer Spectroscopy shows that these sediments have important amounts of jarosite-group minerals and abundant small particle Fe-oxyhydroxides (SPO), mostly ferrihydrite. The sediments down to the mixing zone also have minor quantities of pyrite \pm sphalerite. Beyond the mixing zone, sulfides disappear and SPO dominate, while jarosite has a minimum precisely at the mixing zone. Some hundreds of meters downstream schwertmannite was also detected. These findings suggest that the waste water input is actually promoting the reductive dissolution of jarosite and SPO from the stream bed sediments at the mixing area releasing the metals adsorbed onto these phases back into solution. Subsequent Fe hydroxide precipitation and the metastable nature of schwertmannite sustain an acid environment in spite of the feeding waters having a pH above 8. This maintains metals in solution, with the exception of As that is adsorbed on the newly formed Fe-hydroxides along the stream path. All other elements arrive at the discharge point of the stream 10 km away with the same concentration in solution as when they started at the mixing zone.

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