Contamination of waters related to abandoned W-Sn mines (Murçós, NE Portugal)

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The mining activity contributed well to the Portuguese economy. Although about ninety Portuguese abandoned mining areas are known to be contaminated, only a few of them have received environmental remediation.

The Murçós mining area is located at Galiza-Trás-os-Montes Zone, northeastern Portugal. The W-Sn mineralization is of stockwork type. The main W-Sn quartz veins intersect Silurian schists and the Variscan biotite granite. The W-Sn quartz veins contain mainly scheelite, cassiterite, wolframite, pyrite, arsenopyrite, sphalerite, chalcopyrite, galena, rare pyrrhotite, stannite, native bismuth, joseite, bismuthinite, matildite, anglesite, scorodite and roosveltite. The exploitation of scheelite and cassiterite took mainly place at the surface in four open pit areas between 1948 and 1976 and produced 335 tons of W and 150 tons of Sn. Three lakes were formed as a result of the mine exploitation. Remediation processes were performed between 2005 and 2007 and included the confination and control of tailings and rejected materials and fitoremediation with macrophytes. This abandoned mining area is located close to a rural area and some of the waters are used for agriculture and others for human consumption. Ten sampling points were selected, three in the pit lakes and seven in the surface waters. Waters from the pit lakes are acid (pH = 4.03 - 5.88), have the highest electrical conductivity value (343 μS/cm) and SO_4^{2-} (194 ppm), Ca (44 ppm), Mg (15 ppm), Mn (2.6 ppm), Al (8.6 ppm), Zn (0.6 ppm), Ni (0.1 ppm) and Co (0.1 ppm) contents, but with a low metal content. The surface waters are near-neutral with a low metal content. Most waters are of mixed type and some of calcium-sulfatated type. Most waters from Murçós area must not be used for human consumption and agriculture due to their high As, Fe and NO_2^- contents. Those from the open pit lakes also have contents of Mn, Al, Zn, Cd, Ni and SO_4^{2-}, which show that they must not be used for human consumption and agriculture.

Surface speciation of sulfate at a mineral-water interface

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Surface speciation is important for understanding the adsorption mechanisms and the long-term behavior of dissolved toxic species as well as the bioavailability of nutrients. In addition, the speciation influences the physicochemical property of the minerals, such as solubility of nano particles and dissolution rate of mineral. Ferrihydrite is low crystalline ferric (hydr)oxide widely distributed in soils and rivers. It is also thought to be an effective anion adsorbent because of its high-specific surface area and positively-charged surface in natural water. Sulfate is common anion in soils and rivers. It is reported that sulfate competes with phosphate, carbonate and organic acid adsorption, and the adsorption of trace metals is enhanced in the presence of SO_4 [1]. The present study aims to reveal the surface speciation of sulfate at the electrolyte solution-ferrihydrite interface under various pH and ionic strength conditions by means of *in situ* IR spectroscopy (ATR-FTIR) and surface complexation modeling (Extended Triple Layer Model: ETLM).

IR spectra of sulfate adsorbed on ferrihydrite were fitted by Gaussian functions based on the assignments by Peak *et al.* [2]. The number and position of the peaks from IR spectra showed there are inner-sphere and outer-sphere sulfate complexes. Outer-sphere complex is dominant under the examined pH (4 to 9) and ionic strength (I = 0.01 to 0.1) conditions, although the contribution decreases with increase of ionic strength and decrease of pH. The coordination environment was estimated by ETLM analyses of independent surface charge data of ferrihydrite in electrolyte solutions as function of pH and ionic strength. The coordination environment of outer-sphere species was determined to be $(>FeOH_2^+)_2\_SO_4^{2-}$ (bidentate deprotonated outer-sphere species) while that of inner-sphere species was $>FeOSO_3^-$ (monodentate deprotonated inner-spher species). ETLM prediction using these two sulfate surface species and these reaction equations quantitatively reproduced the surface speciation as function of pH and ionic strength obtained by the ATR-IR analyses.

[1] Fukushi & Sverjensky (2007) *GCA* **71**, 1–24. [2] Peak *et al.* (1999) *J. Colloid Interface Sci.* **218**, 289–299.