

Factors Influencing the Precipitation of Sulphate-rich Iron Oxides, and Their Ability to Adsorb Trace Metals

Jenny Webster (j.webster@auckland.ac.nz)¹, Vincent Lane (vincent.lane@esr.cri.nz),
Richard Howarth (richioo@hotmail.com), Peter Swedlund (p.swedlund@auckland.ac.nz)¹ &
David Saul (dj.saul@auckland.ac.nz)¹

¹ University of Auckland, Private Bag 92019, Auckland, New Zealand

In acid mine drainage (AMD) systems sulphate-rich iron oxides play an important role in adsorbing trace metals, reducing their concentration and bio-availability in the water column. However, it can be difficult to predict the mineralogy of these oxides in AMD, on the basis of geochemistry alone. Natural occurrences of sulphated goethite (alpha FeOOH) and schwertmannite (Fe₁₆O₁₆(OH)₁₀₋₁₁(SO₄)_{3,0-2.5}) can be difficult to reconcile with the precipitating conditions used for abiotic laboratory synthesis. The ability of these oxides to adsorb trace metals is also difficult to predict using existing surface complexation data, which is mainly derived from adsorption studies using pure ferric oxide phases. The active precipitation of abundant sulphated goethite and schwertmannite in close proximity at the former Tui lead-zinc mine in New Zealand, provides an opportunity to better define the natural chemical and microbiological conditions of precipitation, and the adsorption characteristics of these oxides.

Where AMD seeps from the base of the Tui tailings dam, the water has high sulphate and ferrous iron concentrations, and is acidic (pH 3.5) and anoxic. Distinctive spiny schwertmannite crystals are growing on algal filaments at this site, formed by the oxidation of dissolved ferrous iron under these conditions. This process can not be duplicated under abiotic conditions in the laboratory, where sulphated goethite is the predominant phase formed at this pH, unless a starting solution of ferric iron and sulphate is used. Molecular microbiological investigations (amplified ribosomal DNA restriction analyses, used in conjunction with 16S RNA sequencing) suggest that a very limited bacterial population is present, dominated by a single organism. The organism is phylogenetically related to clone TRA3-20, which has previously been described from Iron Mountain in California, USA. It is suggested that these organisms are likely to belong to a new genus of the beta-subdivision of the Protobacteria, and may play a role in the formation of schwertmannite.

Oxide mineralogy changes both with depth within the layered oxides below the tailings dam, and with distance from

the seepage point. A transition from schwertmannite to sulphated goethite is evident, with sulphated goethite being actively precipitated approximately 40 m below the tailings dam seepage. The water here has a similar sulphate content, but is fully oxygenated and acidic (pH 2.9). Dissolved iron concentrations have decreased in response to ferrous iron oxidation and oxide precipitation. Microbial action does not appear to be required for the formation of this oxide, as abiotic oxidation of a ferrous iron and sulphate solution at pH 3.0 does precipitate sulphated goethite. The predominant microbial species identified in a sulphated goethite sample by conventional microbiology was a *Leptospirillum*-like bacteria. However, molecular microbiology has so far failed to find any evidence for the presence of either *Leptospirillum* or *Thiobacillus ferrooxidans* at this site. A mixed oxide sample taken from the interface between schwertmannite and sulphated goethite showed a more diverse bacterial population, with cloned 16S RNA gene sequences affiliated to members of the gamma-Protobacteria and acidobacteria. Organisms related to clone TRA3-20 were again observed.

Trace metal adsorption edges for copper and zinc adsorption on abiotic synthetic, and biotic natural (freeze-dried), oxide analogues of sulphated goethite or schwertmannite are similar. Small discrepancies are consistent with differences in surface area. Under acid conditions, the adsorption of copper and zinc is enhanced on schwertmannite relative to ferrihydrite, and on sulphated goethite relative to pure goethite. This is particularly evident for copper adsorption on sulphated goethite. Surface complexation constants for ternary complex formation (i.e., FeOHMeSO₄) have been derived from the experimental adsorption data, and enable accurate predictions of copper and zinc adsorption onto schwertmannite to be made. The high degree of copper and zinc adsorption on sulphated goethite remains difficult to explain. It does, however, suggest that AMD treatment systems designed to precipitate this oxide as a "designer adsorbent", would remove copper and zinc more effectively than conventional treatment systems using pure goethite or ferrihydrite adsorbents.