The life cycle of nanoparticles in Acid Mine Drainage: An *in-situ* synchrotron study

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Owing to their high surface area and increased surface reactivity, iron oxyhydroxide nano-phases in natural and contaminated environments play an important role in many processes which control the cycling and bioavailability of trace contaminants (e.g As). Schwertmannite (SW), a poorly-ordered iron oxyhydroxy-sulphate that typically forms in low pH (2.5 < pH < 4.5), high [SO4] aqueous environments (i.e., Acid Mine Drainage, AMD), is known to effectively remove toxic species from solution. However, the pathways leading to its formation and crystallisation have so far not been quantified. Here we present new data using in-situ time-resolved synchrotron-based Small Angle X-ray Scattering (SAXS) and Energy Dispersive X-ray Diffraction (EDXRD) to characterise the nucleation, growth, and transformation of schwertmannite.

A solution-SAXS technique utilising a rapid-mixing, stopped-flow cell was developed, which permits solution mixing and subsequent in-situ and real-time quantification of SW nanoparticle nucleation and growth rates and, consequently, mechanistic information and the effects of co-precipitation with arsenate to be determined. Our data show that the SW critical nucleus is ~ 6 Å and that the particle radius increases to ~20 Å in 600 s. Kinetic analysis indicates a surface incorporation mechanism with a first-order dependence on reactant concentration. Arsenate is shown to inhibit precipitation rates by blocking growth sites on the particle surface.

To compliment our results we employed cryo-TEM and RAMAN to investigate the structure and particle size of the reaction end products. The images and spectral information obtained show, for the first time, the primary SW particles in their dispersed state (= 5nm Ø particles) and are in agreement with our SAXS data.

Time-resolved, in-situ, EDXRD was used to determine the kinetics and mechanisms of schwertmannite transformation to a fully crystalline product (e.g. goethite), and to assess the effect of trace elements (e.g. arsenate) on the tranformation process. Experiments at high pH (13.1) show goethite crystallises at lower temperatures (i.e. 70ºC) with hematite becoming increasingly dominant at higher temperatures. The presence of arsenate also stabilises hematite relative to goethite and retards the rate of crystallisation.