

## **Roles of Arsenate and Phosphate in the Nucleation and Growth of Iron (III) (hydr)oxides**

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Iron(III) (hydr)oxides are important in the geochemical cycling of contaminants in aquatic systems. Iron(III) (hydr)oxides can form during the oxidative dissolution of Iron(II) minerals, e.g., pyrite, in acidic environmental systems, such as acid mine drainage. Initial precipitates can be amorphous and poorly crystalline, and thus have a high specific surface area. This property makes them powerful sorbents for water-borne trace metal and metalloid contaminants and organic pollutants. This ability of iron(III) (hydr)oxides to immobilize contaminants is related to whether the precipitates are formed heterogeneously, on mineral surfaces, or homogeneously, in solution.

To evaluate the interactions between newly forming iron (III) (hydr)oxides and environmentally important anions, such as arsenate and phosphate, we studied *in situ* heterogeneous iron(III) (hydr)oxide nucleation and growth on quartz in the presence of these anions. We utilized synchrotron-based grazing incidence small angle X-ray scattering (GISAXS) with other complementary techniques. In a system containing  $10^{-5}$  M arsenate, nanoparticles' radii of gyration ( $R_g$ ) grew to about three times bigger compared to an iron(III) only system, reaching to  $6.1 \pm 0.5$  nm within 1 hr. For a system containing  $10^{-5}$  M phosphate,  $R_g$  reached to  $4.0 \pm 0.2$  nm, which is twice as big as an iron (III) only system. Interestingly, while systems containing these oxyanions had more growth, a system containing only iron(III) had the most nucleation on substrates. *Ex situ* thermal gravimetric analysis and high resolution X-ray diffraction of nanoparticles indicated that precipitates in the arsenate system had the highest water content and that oxyanions may bridge iron(III) hydroxide polymeric embryos to form a structure similar to ferric arsenate or ferric phosphate.

Differences in nucleation and growth rates and particle sizes which induced by the presence of anions will impact the number of available reactive sites, affecting the reactivity of newly-formed particles toward aqueous contaminants. The water content in newly formed nanoparticles can affect their phase transformation and reactive sites.