

Redox-induced nucleation and growth of goethite on synthetic hematite nanoparticles

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ABSTRACT

The iron (oxyhydr)oxides hematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$) are natural and reactive minerals common in soils and sediments, and their adsorption of Fe(II) produces reactive surface sites that facilitate reduction of oxidized environmental pollutants. Single-exposure experiments with 4-chloronitrobenzene showed that hematite is more reactive than goethite, when normalized by surface area loading. Interestingly, the product of Fe(II) oxidation is a mixture of goethite and hematite, and the goethite to hematite ratio depends on the distribution of Fe(II) activated surface sites, which is a function of aqueous Fe(II) concentration, surface area loading, and pH. More goethite is produced under conditions of higher Fe(II), lower surface area loading, and higher pH. Recurrent-exposure experiments showed a substantial decrease in reaction rate after one to three exposures, a trend suggestive of reaction contributions from the increasing goethite surface area over time. Using known atomic surface geometry for goethite and hematite, the hematite {012} facet is proposed as the site of primary mineral growth with goethite {021} at the interface between the two minerals. These results have implications in contaminant fate modeling, where the mineral phases present in the environment, the minerals likely to form, and the surrounding aqueous conditions all have an impact on contaminant reaction rate.

Keywords: Goethite, hematite, oxidative growth, evolving reactivity, Fe(II); Nanominerals and Mineral Nanoparticles