

SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF NANOPARTICULATE GOETHITE

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RESEARCH OBJECTIVES

Nanoparticles feature high surface areas, a tendency to remain in suspension, and differences in their chemical/physical properties relative to bulk phases. As a result, the reactivity of nanoparticles to metal contaminants (e.g., As, Cu, Hg, Zn) may be greatly enhanced in inverse proportion to their size. The objectives of this research are to study the formation, growth, and reactivity of nanoparticulate goethite (α -FeOOH), one of the most common mineral phases in the environment and one of the most reactive in terms of metal-contaminant uptake.

APPROACH

Our approach involves the synthesis and characterization of nanoparticulate goethite over a range of sizes (from 10 to 100 nm). Studies of goethite nanoparticle growth over time are then paired with metal uptake studies and analysis of metal speciation at the mineral-water interface to understand any changes in reactivity as a function of size. Transmission electron microscopy (TEM), surface area analysis, x-ray diffraction (XRD), and dynamic light scattering (DLS) are used to characterize the differently sized batches of nanoscale goethite and determine their size, morphology, surface area, and size distribution. The growth and structure of the nanoparticles are investigated through small- and wide-angle x-ray scattering (SAXS/WAXS) spectroscopy, while metal uptake is studied using batch sorption experiments paired with inductively coupled plasma-atomic emission spectrometry (ICP-AES) and extended x-ray absorption fine structure (EXAFS) spectroscopy.

ACCOMPLISHMENTS

We have synthesized goethite over a range of 10–80 nm in diameter (surface areas >250 m²/g), using a microwave annealing process and aging at 90°C. The size distribution of the nanogoethite has been characterized with DLS and TEM. Analyzing aged samples with DLS shows that the nanogoethite exhibits two stages of growth (Figure 1): relatively rapid growth from 0 to 4 days (10–58 nm) and much slower growth from 4 to 33 days (58–78 nm). This may represent initial evidence of (oriented) aggregation as a mechanism for nanoparticle growth, in agreement with recent studies indicating that growth through aggregation dominates over growth from solution. This distinction is important in predicting the eventual fate/sequestration of metals that may sorb to nanoparticles during their growth.

The SAXS/WAXS spectroscopy work has focused on the *in situ* growth of nanoparticulate goethite suspensions at 90°C.

Batch uptake experiments and corresponding EXAFS analysis have shown differences in the mode of metal speciation between 10 nm and 73 nm batches of goethite, indicating that there is a particle-size dependency on the method of metal sorption, perhaps caused by varying densities or proportions of sorption sites as a function of size.

SIGNIFICANCE OF FINDINGS

This work has important, fundamental implications for our understanding of how the properties of nanoscale materials, including reactivity to metals, may deviate with decreasing particle size. In addition, this research has potential applications in remediation of abandoned mines or industrially polluted regions, where high-surface-area, hypersorbent phases such as nanoparticulate goethite may assist in the cleanup of heavy metals.

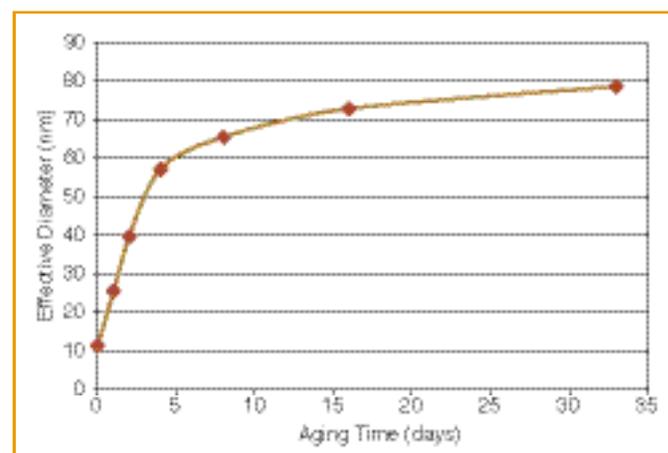


Figure 1. Dynamic light scattering (DLS) measurements tracking the growth of goethite nanoparticles as a function of aging time at 90°C.

RELATED PUBLICATION

Waychunas, G.A., Structure, aggregation, and characterization of nanoparticles. In *Nanoparticles and the Environment* (J.F. Banfield and A. Navrotsky, editors), Mineralogical Society of America, 2001.

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