

Reactivity of iron oxyhydroxide nanoparticles with heavy metals as a function of particle size

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Nanoparticles of inorganic mineral phases are widespread in aqueous environmental systems and can play a significant role in the natural cycling of heavy metals and semi-metals. In particular, iron oxyhydroxides are present in many natural environments as dispersed and/or aggregated nanoparticles covering a wide range of sizes. However, the effects of particle size on heavy metal uptake, especially during nanoparticle aggregation and growth, are not well understood yet hold significant implications for contaminant sequestration and mobility.

To study the effects of particle size on metal uptake, a series of iron oxyhydroxide batches ranging from 5-80 nm in average diameter was synthesized using a rapid microwave technique followed by aging in suspension at 90°C. Selected iron oxyhydroxide nanoparticle suspensions of 5, 25, and 75 nm in effective diameter were then exposed at pH 6 to 0.5 mM concentrations of As(V), Cu(II), Hg(II), and Zn(II), metal(loid) contaminants frequently associated with acid mine drainage systems.

EXAFS spectroscopy of the resulting solids shows that while metal speciation on the 25- and 75-nm particles is identical (suggesting direct inner-sphere bonding), uptake to the 5-nm particles displays slightly longer (0.1-0.3 Å) second-neighbor metal-iron distances. This suggests distortion and/or disordering of the Fe(O,OH)₆ octahedra which comprise the structure of iron oxyhydroxides. It is also consistent with the oblong morphology and greater degree of surface curvature observed in the 5-nm particles through TEM microscopy, with particles becoming more tabular/acicular as particle size increases (25-, 75-nm).

Macroscopic uptake curves were generated using the same nanoparticle batches and metal contaminants over a concentration range of 5-1000 µM. Results show that the smallest particles exhibit greater overall uptake (due to higher surface areas) yet have reduced surface loadings (expressed in µmol/m²) relative to larger particles. Thus there are observable differences in both the extent and mode of metal uptake onto iron oxyhydroxides which appear to be largely dependent on size and morphology at the nanoscale.

Nanoscience meets geochemistry: Size-dependent reactivity of hematite

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Geological materials at the nanoscale, typically considered to be approximately 1-100 nm, are extremely common. Nanoscience explores how the properties of nanoscale materials change as a function of size. Consequences of these size-dependent property changes for the geochemical reactivity of nanoscale materials in the environment remain almost entirely unexplored. Results will be presented involving the size-dependent reactivity of synthetic (7 nm, 9 nm, and 40 nm average diameter), commercial (NANOCAT 3 nm, MACH-1, Inc.), and natural (150-250 nm ground fraction) hematite and hematite-like materials. In this study, the reactivities of these particles is tracked using heterogeneous manganese oxidation rates and photochemical reactivity. Dramatic size-dependent reactivity is observed and rationalized in both systems.

Initial rates of heterogeneous manganese oxidation on synthetic 7 nm, 9 nm, and 40 nm hematite in the presence of oxygen decrease by approximately 1-2 orders of magnitude as the average particle diameter increases, when normalized to surface area. This size-dependent rate change is hypothesized to result from changes in metal coordination environment and surface chemistry.

In additional experiments, photochemical release of ferrous iron has been measured experimentally upon UV illumination in pH 4.0 oxalate (0.005 M) solutions. Surface area normalized release of ferrous iron from synthetic 40 nm and natural ground 150-250 nm hematite are very similar. Release was approximately two orders of magnitude greater for 3 nm NANOCAT material and approximately one order of magnitude greater for 7 nm and 9 nm synthetic hematite. Previous researchers have found photochemical reduction of bulk hematite to be relatively inefficient; electron-hole pairs recombine after an average diffusive length of a few nanometers. As the dimensions of the particles approach this length, trapping of electrons at the particle surface (as Fe²⁺) is expected to compete significantly with recombination.