

Influence of iron oxide nanoparticle crystallite size on the sorption and reduction of plutonium

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Plutonium is present in the environment due to nuclear weapons production and testing and poses a long-term threat to public health because of its radiological toxicity and long half-lives.¹ The primary factor in determining the mobility of plutonium in the subsurface environment is oxidation state. While Pu(IV) is generally assumed to be the least mobile oxidation state and Pu(V) the most mobile oxidation state, certain caveats exist (i.e., nanoparticle-facilitated transport).¹ Mineral nanoparticles have diameters between 1 nm and 100 nm, have unique properties that differ from bulk material, and are ubiquitous in natural environments.^{2,3} Previous studies report that decreasing the crystallite diameter of mineral nanoparticles can impact the chemical behavior of metal contaminants due to the increased chemical reactivity and surface area that occurs at smaller nanoparticle diameters.² Thus, we hypothesize that iron oxide nanoparticles will increase the sorption and reduction of Pu, relative to bulk mineral counterparts, due to the presence of more undercoordinated sites at the nanoparticle surface. To test this hypothesis, we conducted batch sorption experiments with hematite (α -Fe^{III}₂O₃) and magnetite (Fe^{II}Fe^{III}₂O₄) nanoparticles as a function of nanoparticle diameter (8, 40, 60 nm, and bulk) under environmental conditions (e.g., $I = 0.1$ M NaCl, pH = 8, [Pu(V/VI)]_i = $1.02 \cdot 10^{-5}$ M) and for some experiments, the resulting solid phases were analyzed using Pu M₄-edge high-energy resolution fluorescence detection x-ray absorption near-edge structure (HERFD-XANES) spectroscopy. We observed an increase in sorbed Pu (mg kg⁻¹) with decreasing nanoparticle diameter, which is attributed to the high surface area of the nanoparticles yet found that the Pu sorption density (mol m⁻²) was constant across all samples. HERFD-XANES analysis showed that Pu was reduced to Pu(IV) on the nanoparticle surfaces. The results of these experiments will lead to an increased understanding on role of particle size on Pu sorption and reduction and, ultimately, how these effects impact the chemical behavior of Pu at the mineral-water interface.

(1) Hixon, A., et al., *Environ. Sci. Process. Impacts* **2018**,