

## Iron-Laden Mineral Colloids as Naturally Abundant Catalysts for Peroxide-Based In Situ Chemical Oxidation

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**Background/Objectives.** Mineral surfaces play an important role in catalyzing contaminant redox transformations. Iron-laden mineral colloids are of particular interest to environmental researchers because of their natural abundance in the aquatic environment and their significant catalytic activity in generating reactive oxygen species. The latter has direct implications for the design and implementation of in situ chemical oxidation (ISCO) for contaminated site remediation. Although various forms of iron oxides have been studied as catalysts in hydrogen peroxide-based ISCO systems, little attention has been paid to the catalytic activity of iron attached to background colloids such as silica and aluminosilicates. This study aims to investigate the activity of silica and alumina whose surfaces are deposited with iron species as model colloids for hydrogen peroxide ( $H_2O_2$ ) activation and hydroxyl radical generation. We aim to identify critical factors affecting the structure and reactivity of iron-laden surfaces, so that the intrinsic catalytic activity of natural abundant colloids in ISCO implementations can be quantified.

**Approach/Activities.** Synthetic silica ( $nSiO_2$ ) and alumina ( $nAl_2O_3$ ) nanoparticles were used as model colloids and these particles were immersed in dilute aqueous solutions of Fe(II) or Fe(III) to simulate the natural processes of iron deposition. The activity of Fe-laden particles for  $H_2O_2$  activation and hydroxyl radical formation was examined using benzoate as a probe compound within a pH range of 4 to 7. A subset of particles was immersed in an aqueous environment for an extended period (58 days) to evaluate possible changes in surface chemistry and reactivity with prolonged aqueous aging. The morphology, molecular structure, and ligand environment of the surface Fe species were examined using various microscopic (TEM and AFM) and spectroscopic (Mossbauer spectroscopy and Diffuse Reflectance UV-Vis spectroscopy) techniques.

**Results/Lessons Learned.**  $nAl_2O_3$  exhibited higher surface uptakes of aqueous Fe(II) and Fe(III) than  $nSiO_2$ . All Fe-laden particles showed evident reactivity for  $H_2O_2$  activation, and particles exposed to Fe(II) solutions showed higher reactivity than those prepared in Fe(III) solutions. For the same type of mineral colloids, the rate of  $H_2O_2$  conversion to hydroxyl radical increases with the amount of Fe deposited on the surface until a critical surface Fe loading was reached. Solid characterization with Diffuse Reflectance UV-Vis spectroscopy suggests the critical surface Fe loading corresponds to a transition from iron deposition via predominantly surface adsorption to surface precipitation. Consistent with earlier studies of  $H_2O_2$  activation on heterogeneous Fe catalysts, increasing pH slowed down the rate of hydroxyl radical production. On-going experiments suggest that freshly deposited Fe species have higher catalytic activities than those aged in aqueous environment (data acquiring at the time of abstract submission). Therefore, while the results of this study confirmed significant activity of the iron-impregnated colloids in the  $H_2O_2$ -based ISCO reactions, the rate and efficiency of reactive oxidant formation depend strongly on the structure and coordination environment of the surface Fe species, which are influenced by aqueous and mineral surface chemistry and iron deposition history.