The Influence of Calcium Carbonate Grain Coatings on Contaminant Reactivity in Vadose Zone Sediments

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Research Objectives

Fundamental research is proposed to investigate the role of calcium carbonate grain coatings on the vadose zone chemical reactivity of key Hanford contaminants (i.e., $^{60}Co^{2+}$, $^{90}Sr^{2+}$, CrO_4^{2-}, and $^{99}TcO_4^{-}$). Calcium carbonate is widely distributed through the Hanford vadose zone as a result of current and past geochemical processes, and exists as grain coatings and intergrain fill. It also results from the interaction of high level waste (e.g., high in Na^+ and OH^-) with Ca-saturated subsurface sediments. While secondary iron-, aluminum-, and manganese-oxyhydroxide grain coatings are known to control the sorption chemistry of non-calcareous sediments for inorganic ions, no comparable understanding exists for carbonate grain coatings, which may be equally or more abundant in certain situations. We hypothesize that carbonate coatings enhance the sorption of carbonate compatible contaminants (e.g., ^{90}Sr, ^{60}Co) through a combination of adsorption and co-precipitation processes, but interfere with the reductive immobilization of the oxoanions CrO_4 and TcO^{4-} by passivating electron dense surfaces of Fe^{2+}- minerals such as magnetite and biotite in Hanford sediments.

This project will explore the behavior of calcium carbonate grain coatings including how they form and dissolve (e.g., natural and waste fluid induced), their reactivity toward contaminants under water-saturated and unsaturated conditions, their impact on the reactivity of the mineral substrate, and their in-ground composition and minor element enrichment. The goal is to provide an improved understanding of contaminant sequestration/immobilization reactions that can be scaled to macroscopic reactive transport models used to forecast contaminant migration. Our scientific focus will be on the influence of the coatings on, 1.) surface coordination or co-precipitation reactions, and 2.) electron transfer reactions that can result in the immobilization of redox-sensitive contaminants. Modern surface- and bulk-sensitive structural and imaging methods including X-ray absorption spectroscopy, scanning probe microscopy, photoelectron spectroscopies, and others will be applied in concert with judiciously designed model systems such as epitaxially grown surfaces of known crystallographic orientation and structure to provide a rigorous molecular and microscopic understanding of the controlling reactions of target contaminant ions with carbonate-coated mineral surfaces. Model system studies will be linked with parallel spectroscopic, microscopic, and macroscopic investigations of calcareous Hanford sediments, to provide basic scientific information for the remediation/closure of Hanford and other DOE sites.