Spectroscopic and Microscopic Characterization of Contaminant Uptake and Retention by Carbonates in Soils and Vadose Zone Sediments

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Dr. Richard J. Reeder, SUNY at Stony Brook

Research Objectives

The release and migration of toxic metals and radionuclides in the soil and vadose zones at various sites over the DOE Complex pose serious technological challenges, including the design and implementation of cost-effective remediation strategies. This requires knowledge of the factors that govern contaminant mobility and reactivity within their host materials. Pedogenic calcium carbonate is a locally important component of soils and vadose-zone materials at the Hanford Site, where it coats grains and occurs as a massive caliche layer at depth. This project examines the reactions and uptake behavior of toxic metals and radionuclides present in soils and vadose-zone sediments containing calcium carbonate.

The main research objective is to assess the effectiveness of uptake and retention of selected contaminants (Co, Cs, Pb, Sr, and Cr) on calcium carbonate (calcite), with a focus on conditions and materials relevant to the Hanford Site. This includes detailed microscopic and spectroscopic characterization of carbonate coatings and caliche from the Hanford Site, combined with experimental determination of the uptake behavior of selected contaminants on calcite surfaces and consideration of factors influencing uptake behavior and retention. This will rely on microscopic, mineralogical, and geochemical characterization of natural materials, as well as spatially resolved X-ray fluorescence (micro-XRF) and X-ray absorption fine structure (XAFS) spectroscopy of uptake products. The expected results will have direct application for assessing the role that calcium carbonate phases play in sequestering toxic metals and radionuclides at the Hanford Site.

Research Progress and Implications

This section summarizes work completed after 6 months of a 3-year project. Preliminary findings relate to two specific areas: coprecipitation of CrO$_4^{2-}$ with calcite and reaction of Pb$^{2+}$ and Sr$^{2+}$ containing solutions with natural caliche samples from the Pasco Basin area. These findings are necessarily preliminary in nature. Controlled laboratory coprecipitation of CrO$_4^{2-}$ with calcite shows that CrO$_4^{2-}$ is discriminated against during crystallization, i.e., the $K_d < 1$ for CrO$_4^{2-}$ incorporation with calcite. Experiments on calcite single crystals, however, reveal a strong surface control on $K_d$. In particular, the distribution and availability of different surface sites on calcite, results in differences in uptake that may be as large as a factor of 5. This suggests that the nature of the carbonate surface plays an important role in the extent to which CrO$_4^{2-}$ is removed from soil and vadose-zone fluids when calcite is forming. Current work assesses the role of crystallization rate on uptake behavior.

Experiments have also been initiated to assess the interaction of Pb$^{2+}$ and Sr$^{2+}$ containing solutions with natural caliche from selected locations in the Pasco Basin area. These caliche samples share many characteristics with those found in Hanford Site sediments. Initial results indicate a strong but spatially heterogeneous interaction of Pb$^{2+}$ with calcite. This suggests that only a small proportion of the caliche surface offers favorable reactive sites for Pb$^{2+}$ uptake. Current work is aimed at characterization of the mechanism of uptake. Sr$^{2+}$ interaction is also observed, but the presence of Sr in the caliche complicates characterization. Further work is underway to address these problems.
Planned Activities

Future activities call for both adsorption and coprecipitation studies of selected metal species with calcium carbonate. Systematic adsorption and desorption behavior will be studied using radiolabeled metals and gamma spectroscopy. X-ray absorption fine structure (XAFS) spectroscopy will be used to characterize the local coordination of metal species during and following uptake experiments. Spatially resolved X-ray fluorescence and X-ray absorption spectroscopy (micro-XRF/XAS) will be used to map the distribution of contaminant reaction products after exposure to natural carbonate substrates in parallel experiments. Separate coprecipitation experiments with selected contaminant metals will allow an assessment of the effectiveness of uptake during crystallization of calcite, which may be favored in the soil and vadose zone as a result of periodic wetting and drying, and also in response to the highly alkaline waste fluids. XAFS spectroscopy will again be used to confirm speciation with the solid calcium carbonate.