Calcite Precipitation and Trace Metal Partitioning in Groundwater and the Vadose Zone: Remediation of Strontium-90 and Other Divalent Metals and Radionuclides in Arid Western Environments

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Research Objectives

Radionuclide and metal contaminants are present in the vadose zone and groundwater throughout the U.S. Department of Energy (DOE) weapons complex. Demonstrating in situ immobilization of these contaminants in vadose zones or groundwater plumes is a cost-effective remediation strategy. However, the implementation of in situ remediation requires definition of the mechanism that controls sequestration of the contaminants. One such mechanism for metals and radionuclides is co-precipitation of these elements in authigenic calcite and calcite overgrowths. Calcite, a common mineral in many aquifers and vadose zones in the arid western U.S., can incorporate divalent metals such as strontium, cadmium, lead, and cobalt into its crystal structures by the formation of solid solutions. The rate at which trace metals are incorporated into calcite is a function of calcite precipitation kinetics, adsorption interactions between the calcite surface and the trace metal in solution, solid solution properties of the trace metal in calcite, and also the surfaces upon which the calcite is precipitating. A fundamental understanding of the coupling of calcite precipitation and trace metal partitioning and how this may occur in aquifers and vadose environments is lacking.

The focus of the research proposed here is to investigate the facilitated partitioning of metal and radionuclides by their co-precipitation with calcium carbonate. Our specific research objectives include

- Elucidating the mechanisms and rates of microbially facilitated calcite precipitation and divalent cation adsorption/co-precipitation occurring in a natural aquifer and vadose zone perched water body as a result of the introduction of urea.
- Assessing the effects of spatial variability in aquifer host rock and the associated hydro/biogeochemical processes on calcite precipitation rates and mineral phases within an aquifer and a vadose zone perched water body.

Research Progress and Implications

This report summarizes project activities after 5 months of a 36-month project. Water samples were collected from wells in the Eastern Snake River Plain Aquifer (SRPA); three were located on the INEEL and one just south of the site boundary. All groundwater samples tested positive for urease activity, in both liquid and solid media. Other groundwater samples collected from elsewhere in eastern Idaho also universally tested positively, indicating that urease activity is indeed common in the SRPA. Twelve ureolytic SRPA isolates were obtained from the urea agar plates. Fatty acid methyl ester (FAME) profiles were obtained for all twelve isolates. Principal component analysis of

FAME results indicated that the isolates could be divided into three main groups. Based on these results, one member of each group was selected for further characterization. All three of the isolates were gram negative rod-shaped heterotrophs, but the carbon source utilization potential results indicated differences between the isolates. However, for all three organisms amino acids appeared to be oxidized most rapidly. Limited phylogenetic analysis performed on the isolates indicated that all three likely had 16S rRNA gene sequences very similar to previously described isolates or clones. Because the partial gene sequences obtained for the SRPA isolates were so similar to previously reported sequences, the acquisition of sequence data for the entire 16S rRNA gene was not pursued further.

The ability of SRPA isolates to hydrolyze urea and precipitate calcite was demonstrated in batch experiments. Cells used in the calcite precipitation experiments were already induced for urease expression, and upon initiation of the experiments the hydrolysis of urea was confirmed by the immediate increase in pH and the production of ammonium. By the end of the eight-hour experiment, the pH in all of the cultures reached similar values, around pH 8.3-8.5. Experimental result suggests that the urease activity in the SRPA isolates is significantly lower than in the *Bacillus pasteurii* reference culture. In all cases however the ammonium concentrations increased linearly with time in the experimental cultures.

In all of the cultures, visible white precipitates developed within the first half-hour after inoculation. This was consistent with geochemical modeling using MINEQL, which predicted that while the medium was initially almost two orders of magnitude under-saturated with respect to calcite, the introduction of less than 1 mM $(NH_4)_2CO_3$ would cause calcite supersaturation. Based on the measured ammonium production rates, this supersaturation likely occurred within the first 12 to 24 minutes of culture growth. The identity of the precipitates as calcite was confirmed by X-ray diffraction. Scanning electron microscopy revealed both spherical and amorphous morphologies, with microbes in close association with the minerals.

Dissolved calcium measurements also confirmed the transfer of calcium into the solid phase. The production of ammonium was correlated with the precipitation of calcite. Comparison of MINEQL predictions for the expected drop in dissolved calcium concentration as a function of ammonium concentration with actual measured values from the experiments imply that dissolved calcium concentrations were controlled effectively by the equilibrium solubility of calcite. The results indicate that the generation of two moles of ammonium (or the hydrolysis of one mole of urea) results in the removal of one mole of calcium from solution. This corresponds to the reaction:

$$H_2NCONH_2 + 2H_2O + Ca^{2+} \rightarrow 2NH_4^+ + CaCO_3$$

In this system then, the rate of calcite precipitation is directly linked to the rate of urea hydrolysis. For field application of the proposed remediation technology, the demonstration of a direct link between the urea hydrolysis and calcite precipitation reactions will be important, because it will not be possible to recover and accurately quantify calcite precipitates from the subsurface. Rather, it will be necessary to confirm and monitor urea hydrolysis and pH, as indirect evidence that carbonate mineral precipitation is occurring in the aquifer as a result of the introduction of urea.

The results of our preliminary evaluation of the potential for utilizing urea hydrolysis as the basis for an in situ remediation technique for ^{90}Sr and other divalent contaminants in SRPA groundwater are promising. Urea hydrolyzing organisms are common in the aquifer, and they can catalyze precipitation of calcite similarly to the known urease positive organism *B. pasteurii*.

Planned Activities

During the remainder of the first year of this project experiments under conditions more closely simulating natural SRPA groundwater will be conducted to determine whether the observations derived in this study are applicable to environmental conditions. In addition, experiments including trace levels of strontium and or uranium are planned. Preliminary results suggest that the incorporation of trace metals significantly influences the morphology of the precipitated calcium carbonate and in the case of strontium can result in the formation of aragonite rather than calcite. During the second year an in situ experiment is planned in a single groundwater well at the INEEL.

Information Access

R.D. Lawson, Y. Fujita, F.G. Ferris, F.S. Colwell, and R.W. Smith, "Microbially Accelerated Calcium Carbonate Precipitation for Radionuclide Sequestration: Preliminary Laboratory Evaluations of Urea-Hydrolyzing Organisms (abs.)," Amer. Geophys. Union Fall Meeting 1999 *EOS* **80**:H31B-06 (1999).