

## Annual Progress Report -- EMSP Project 70146

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

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### Research Objective

Historical releases and subsequent migration of toxic metals and radionuclides within the soil and vadose zone at various sites over the DOE Complex pose serious technological challenges, including the design and implementation of cost-effective remediation and/or monitoring strategies. This requires knowledge of the fundamental processes that govern contaminant mobility and reactivity with their host materials. The main research objective of this project is to assess the effectiveness of uptake and retention of selected contaminants (Co, Cs, Pb, Sr, U, and Cr) on calcium carbonate (primarily calcite), with a focus on conditions and sorbent 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. The methodology relies on spectroscopic, microscopic, mineralogical, and geochemical characterization of natural and analog materials, including spatially resolved X-ray fluorescence (micro-XRF) and X-ray absorption fine-structure (XAFS) spectroscopy of uptake products. A primary goal is to determine the reaction mechanisms that govern contaminant uptake by carbonates. 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 and other locations with calcium carbonate, and will also serve as a baseline for similar studies in more complex systems.

### Research Progress and Implications

This report summarizes work completed after 21 months of a 36-month project. In a previous annual report we described results of contaminant uptake by natural caliche from the Pasco Basin area. The new results described here relate to studies of metal coprecipitation with calcite and adsorption on calcite in model systems. One major accomplishment was completion of a study of  $\text{UO}_2^{2+}$  coprecipitation with calcite. Uranyl is the mobile species of uranium and significant plumes containing uranyl exist at the Hanford Site. Previous work had shown that significant uptake of uranyl could occur via coprecipitation with calcite. Our combined X-ray absorption fine-structure (XAFS) and luminescence spectroscopy study of uranyl-doped calcite demonstrated that disruption of the local structure around U results from laboratory coprecipitation, which we interpreted to indicate decreased stability of the uranyl-containing calcite. This suggests that retention of uranyl by calcite may be limited, and remobilization may be enhanced by greater solubility of the calcite. We also found that a change in the local coordination of the uranyl species occurs during the coprecipitation process. This may reflect a kinetic hindrance for uptake. Results in manuscript form are "in press".

Related studies have focused on the uptake of trivalent actinides by calcium carbonate. For this work, we have used the trivalent lanthanides as chemical analogs.

Parallel spectroscopic studies have used X-ray absorption fine structure and infrared spectroscopy to examine the heterovalent substitution of  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Yb}^{3+}$  into calcite. XAFS results reveal that larger lanthanides Nd and Sm have a 7-fold coordination in the Ca site, whereas smaller lanthanides Dy and Yb have the expected 6-fold coordination typical of the Ca site. The defect coordination of the larger lanthanides raises the possibility that actinides, such as  $\text{Am}^{3+}$ , may attain a similar coordination, which would be expected to have decreased stability. This work is currently "in review" for publication.

We have continued our earlier work on  $\text{Pb}^{2+}$  interaction with calcite by use of model systems. Specifically we have undertaken a comprehensive study of  $\text{Pb}^{2+}$  adsorption on calcite using Pb-210 as a radiotracer. Our preliminary results demonstrate that  $\text{Pb}^{2+}$  sorbs very strongly onto calcite, indicating that calcite should effectively scavenge  $\text{Pb}^{2+}$  from soil and vadose-zone solutions. A likely explanation for the strong interaction of  $\text{Pb}^{2+}$  with calcite is the lone electron pair, which in some systems causes distorted coordination. To test this idea, we have carried out similar studies of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  adsorption on calcite.  $\text{Zn}^{2+}$  shows a preference for tetrahedral coordination and  $\text{Cu}^{2+}$  shows a preference for a Jahn-Teller distorted octahedral coordination. For both species, XAFS results show site-selective uptake on calcite that differs from that shown by  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Fe}^{2+}$ . We now speculate that XAFS investigation of  $\text{Pb}^{2+}$  adsorption on calcite will show similar differences in site-selective uptake.

We are also conducting adsorption studies of  $\text{Cs}^+$  on calcite. The results indicate an extremely weak interaction over a range of pH, which suggest that calcite will be ineffective in the uptake and sequestration of this radionuclide in the soil or vadose zone.

### **Planned Activities**

Future research calls for adsorption studies of uranyl on calcite, which will allow comparison with our coprecipitation work. We will also examine natural uranyl-containing calcite to determine if the distorted coordination is typical in nature. We will also study adsorption of selected trivalent lanthanide species on calcite, the lanthanides being used as analogs for trivalent actinides. Previous work has shown there is very strong uptake by calcite. This work will allow us to assess the relative importance of adsorption and coprecipitation, and offer insight to the likely behavior of actinides.

In a new set of experiments we plan to establish the importance of metal-organic ternary complexes on the uptake process. Our approach will be to study  $\text{Co}^{2+}$  coprecipitation in the presence of humic and fulvic substances. Co is an important radionuclide at several DOE sites. Both batch experiments and XAFS characterization will be used to assess whether uptake is affected by ternary complexes.

The goal of all this planned work is to provide a sound scientific foundation for implementation of remediation and/or monitoring strategies.

### **Information Access**

Various project findings may be viewed at the following web sites:

[http://www.osti.gov/em52/NWS2000\\_Posters/id70146.pdf](http://www.osti.gov/em52/NWS2000_Posters/id70146.pdf)

<http://www.pnl.gov/emsp/presentations/reeder/sld001.htm>

Additional information may be obtained from the Lead P.I. (R. J. Reeder)