

Final Report -- EMSP Project 70146 (DE-FG07-99ER15013) Sept. 1999-April 2003

Project Title: *Spectroscopic and Microscopic Characterization of Contaminant Uptake and Retention by Carbonates in the Soil and Vadose Zone*

P.I.: Richard J. Reeder (SUNY-SB); Co-P.I.s: Nicholas S. Fisher (SUNY-SB), Wayne P. Hess, Kenneth M. Beck (PNNL)

Overview

The research focus of this previous EMSP grant was assessment of the role that carbonate minerals play in the uptake and sequestration of metal and radionuclide contaminants in soils and the vadose zone for conditions relevant to the Hanford Site and other sites in the DOE Complex. The project was a collaboration among researchers at SUNY-Stony Brook and EMSL/PNNL. Carbonates, particularly calcite, are present in the Hanford subsurface as grain coatings, disseminated particles, and dense caliche layers. Calcite is also predicted to be forming beneath leaking tanks. A range of metal and radionuclide species that pose risks at Hanford and other DOE sites were considered, including U(VI), Cr(VI), Cs, Pb(II), and selected lanthanides (as models for trivalent actinides). Batch sorption and co-precipitation experiments of these metals with pre-equilibrated calcite and selected uptake experiments on natural caliche formed the basis for evaluating uptake and retention behaviors. In parallel, spectroscopic methods was employed to determine the mechanisms of metal/radionuclide binding (i.e., adsorption, coprecipitation, surface precipitation) and to assess the effect on the stability of the sorbed species and the potential for remobilization. Our results provide new information that can benefit DOE clean-up methodology and potentially provide new approaches for uptake of selected heavy metals. Results have been reported in 6 peer-reviewed journal articles, and 4 additional manuscripts are in various stages of review or preparation. In the following paragraphs we describe the most important accomplishments of this work through February 2003.

U(VI) Uptake by Calcite: Sequestration Mechanisms and Stability

One of the major focuses in this study addressed the interaction of dissolved U(VI) species with calcium carbonate phases under a broad range of solution conditions. Experiments were designed to simulate uranyl uptake (1) in solutions in bulk equilibrium with calcite (to assess sorption mechanisms) and (2) in solutions over a range of calcite supersaturation and ionic strength conditions, where uranyl co-precipitation dominated uptake. These conditions are relevant to soil and vadose zone environments, such as found at the Hanford Site, and rapid crystallization experiments may provide insight to U(VI) behavior for conditions where interactions of solutions induce calcite crystallization. We used EXAFS, XANES, and luminescence spectroscopies to identify the speciation of uranium in solutions, at the calcite-water interface, and in U co-precipitated samples, thereby providing direct information about the chemical and structural state of sorbed U(VI), as well as providing quantitative uptake systematics that may be used in reactive-transport models.

An important characteristic of the solutions considered in our studies is the moderately high concentration of carbonate and calcium, which are required for calcite saturation or supersaturation at pH values in the range 7.5–9. It is well known that uranyl forms several stable complexes with dissolved carbonate, including the uranyl triscarbonate and biscarbonate anions, $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$, and, depending on the Ca activity, the neutral calcium uranyl triscarbonate complex, $\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_3^0$. The dominance of these species at pH values >6 serves

to increase the solubility of U(VI) in carbonate-containing solutions, and hence its mobility. The increasing dominance of carbonate complexes of U(VI) with increasing solution pH are associated with decreasing U(VI) adsorption on oxides, hydroxides, and silicates (Payne et al., 1998; Pabalan et al., 1998), which has been interpreted to indicate that uranyl carbonate complexes exhibit a low affinity for binding at such surfaces. Carbonate ligands exposed at the surface of calcite, however, may compete effectively for uranyl in solution.

Batch sorption experiments were conducted mainly to assess the significance and mechanism(s) of uranyl binding at the calcite-water interface for solution conditions that are relevant to the soil and vadose zone environments. Because synthetic calcite surfaces are highly reactive in water, the reagent calcite sorbent was pre-equilibrated for 3-4 weeks in solutions through which water-saturated air was bubbled (CO_2 partial pressure of $10^{-3.5}$ atm), with pH converging at 8.3. The pH of other suspensions was adjusted to 7.4 and then allowed to re-equilibrate in order to assess the effect of pH over this range. An isotherm was determined for U(VI) concentrations up to 5 mM (Fig. 1). Clear evidence of precipitation was observed for [U(VI)]

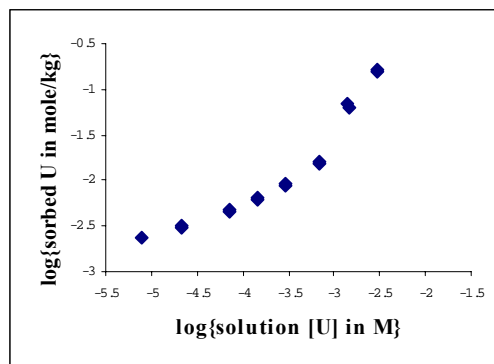


Fig. 1. U(VI) uptake isotherm on calcite at pH 8.3 in pre-equilibrated solutions. For [U(VI)] $> 10^{-3.3}$ M, precipitation was observed.

$> \sim 500 \mu\text{M}$. A distinct EXAFS and luminescence spectrum confirmed the formation of a second U phase for these high U(VI) concentrations, although its identity could not be established. For initial U(VI) concentrations below $\sim 500 \mu\text{M}$, in situ EXAFS and luminescence show the presence of two different U(VI) species bound at the calcite-water interface (Fig. 2). One species is interpreted to be a weakly bound outer-sphere uranyl triscarbonate complex, whereas the second species resembles that observed for U(VI) co-precipitated with calcite. This finding has significance for remediation technologies. Two uptake processes apparently operate on overlapping time scales in these experiments: adsorption and co-precipitation. In the former case, U(VI) weakly adsorbed at the calcite-water interface is potentially labile and sorption is likely reversible, whereas U(VI) incorporated into the solid is less accessible to the solution and therefore more likely to be retained. There is another aspect of these findings that is significant for understanding sorption of contaminants. Contrary to the view that carbonate complexes of U(VI) show little affinity for adsorption, the surface-bound carbonate ligands clearly compete with dissolved carbonate. The K_d values for U(VI) partitioning over the lower U(VI) concentration range are in the range $75\text{--}300 \text{ L kg}^{-1}$.

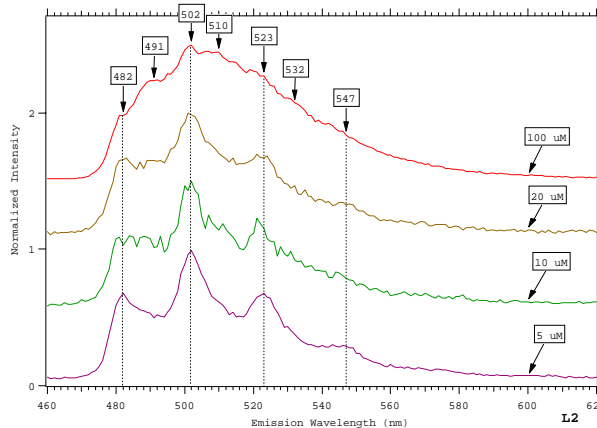


Fig. 2. Luminescence spectra of U(VI) sorbed at the calcite-water interface for a range of initial U(VI) concentrations. The progressive changes in the spectra result from different proportions of multiple species. (Elzinga et al., 2003).

Batch experiments were conducted to examine the uptake of U(VI) via co-precipitation with calcite. Partition coefficients (K_d) for U(VI) coprecipitation in controlled experiments are

less than one, reflecting that the uranyl ion is structurally incompatible with the coordination environments in calcite. However, we observed that K_d values increase as a function of calcite precipitation rate. Hence, rapidly precipitated calcite can take up significant amounts of U(VI). Some final calcite products contained over 2500 ppm U, which could make rapid co-precipitation highly effective as a mechanism for scavenging dissolved U(VI). This has potentially important implications for the remediation techniques using carbonate solutions to mobilize uranium, as supersaturation with respect to calcite may result. Parallel co-precipitation experiments involving the calcium carbonate polymorph aragonite showed significantly enhanced uptake, with final products containing up to 1 wt.% uranium. This supports observations of higher uranium concentrations in natural aragonites compared to calcites.

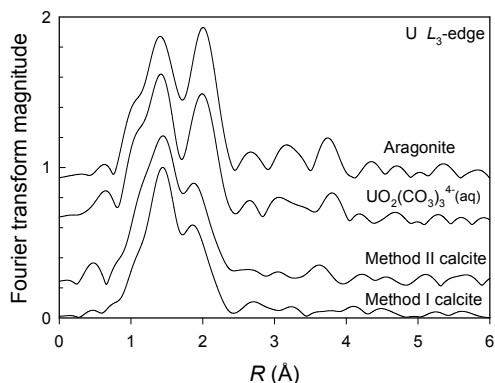


Fig. 3. EXAFS radial structure functions for uranyl incorporated into calcite by two growth methods (bottom), incorporated into aragonite (top), and in the aqueous triscarbonate species. Fitting reveals a disordered local coordination of uranyl in calcite with fewer equatorial oxygens than in aragonite or in the aqueous species (Reeder et al., 2001).

We used a combination of spectroscopic techniques (EXAFS, XANES, luminescence, Raman) to characterize the uranyl species co-precipitated with calcite in order to assess its coordination and stability. Different growth methods were employed, and solution pH, ionic strength, and supersaturation were varied to assess their influence. Steric constraints are believed to hinder isomorphous substitution of UO_2^{2+} in either the Ca or CO_3 sites in calcite. Our spectroscopic results revealed that uranyl incorporated into calcite has a different local coordination than the aqueous uranyl triscarbonate species that dominates the aqueous speciation. In contrast, uranyl incorporated into the CaCO_3 polymorph aragonite has a similar equatorial coordination to the aqueous complex (Fig. 3). We interpreted the equatorial coordination in calcite as having five oxygen ligands, whereas it has six in aragonite and in the aqueous triscarbonate species. EXAFS results showed significant disorder in the coordination shells beyond the first equatorial oxygens, indicating significant disruption of the local environment around the U(VI) substituent. We interpreted this localized structural disruption to indicate a decreased stability of uranyl-containing calcite. Hence, long-term retention of uranyl co-precipitated with calcite is likely to be diminished unless re-structuring or self-annealing results in a more stable coordination.

As noted, the five equatorial oxygens observed for uranyl co-precipitated with calcite differ from the coordination of the aqueous species. Hence we concluded that a coordination change in the equatorial plane must accompany incorporation into calcite. We noted that our previous work showed that uranyl species co-precipitated with aragonite has six equatorial oxygens, with an overall coordination like that of the aqueous species. Hence, no change in equatorial coordination is required for incorporation into aragonite, which we interpreted to be the reason for its larger K_d values.

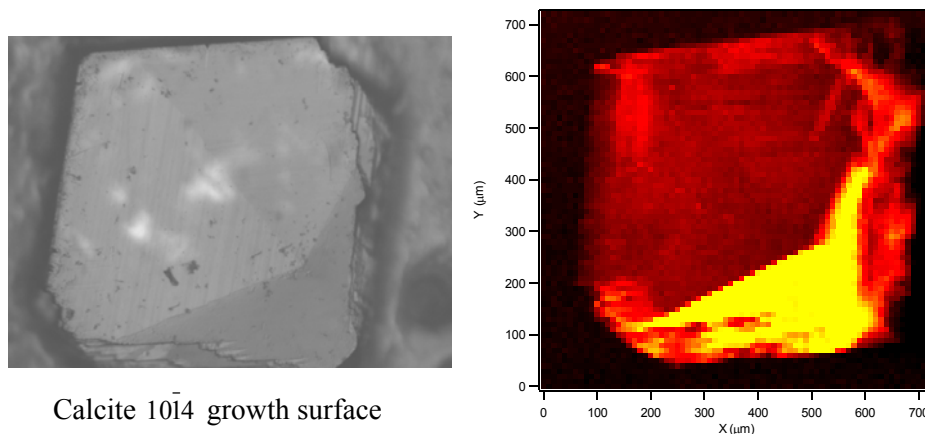


Fig. 4. Differential interference contrast image (above left) of synthetic calcite crystal grown in uranyl-containing solution. The shading patterns show the characteristic development of vicinal surfaces where nonequivalent surface sites are segregated on the face. Synchrotron X-ray fluorescence map (above right) of uranium distribution over the face. Light (yellow) color corresponds to higher U concentration. The U(VI) is strongly partitioned into vicinal surfaces at the lower right, which indicates that uranyl carbonate aqueous complexes show a strong preference for distinct surface sites. Reeder et al., (2001).

Our U(VI) co-precipitation experiments also examined surface site interactions on single crystal surfaces of calcite. We showed that the uranyl triscarbonate species exhibits a distinct preference for uptake among different sites on the common growth form of calcite (Fig. 4). This result parallels other observations showing that Sr, Zn, Co, and Pb are selectively taken up at distinct sites on the calcite surface (cf. Reeder, 1996). This indicates that the overall effectiveness of uptake by calcite will be affected by the availability and density of the preferred sites. Calcite crystal morphology is one important factor that controls site density. Heterogeneous uptake can therefore be expected on calcium carbonate components in soils and vadose zone materials, much in the same way as on clay and mica grains. Our results describing U(VI) uptake and retention by calcium carbonate are reported in two papers (Reeder et al., 2000, 2001a) and were presented as a poster at the EMSP National Meeting. A paper reporting uranyl sorption and precipitation at the calcite-water interface is in review (Elzinga et al., 2003).

Uptake of Lanthanide Species by Calcite and Implications for Trivalent Actinides

Another important research initiative examined uptake of trivalent lanthanide species by calcite. The lanthanides occur dominantly as 3+ species in nature and have been widely studied as analogs for trivalent actinides, such as Am³⁺ and Cm³⁺. The few existing experimental studies indicated that lanthanides and trivalent actinides exhibit a strong affinity for adsorption and coprecipitation with calcium carbonate phases, making these especially effective sorbents for attenuating the mobility of such trivalent species in the soil and vadose zone environments. Our experimental effort focused on coprecipitation and adsorption of selected lanthanides with calcite, the dominant carbonate phase in the Hanford subsurface. We chose to consider Nd, Sm, Dy, and Yb because they span a significant portion of the lanthanide series. Although the trivalent lanthanides exhibit similar chemical behaviors, their most notable difference is the progressive variation in ionic radius across the series, i.e., the lanthanide contraction. All these lanthanides occur dominantly as carbonate complexes in these co-precipitation solutions. Our batch uptake experiments documented extremely high K_d values (> 800) for coprecipitation with calcite. There has been a presumption that substitution occurs at the Ca site, which is in octahedral coordination in calcite. The charge difference associated with the substitution must be accompanied by a

charge compensation mechanism or structural rearrangement, either of which could affect the stability of the lanthanide-bearing calcite. We used EXAFS and optical spectroscopies to determine the coordination of individual lanthanides co-precipitated with calcite. We found that Nd and Sm (the light members of the series with larger ionic radii) occupy a modified Ca site within calcite, having increased oxygen coordination relative to the ideal Ca site (Fig. 5) (Elzinga et al., 2002). In contrast Dy and Yb (heavy members with smaller ionic radii) occupy the Ca site with six oxygen ligands as in the ideal calcite structure. The increased oxygen coordination for the larger Nd and Sm requires localized disruption or a defect-like structure around the lanthanide ion itself. That should result in a decreased stability of Nd- and Sm-containing calcite relative to an ideal isomorphous substitution. This has important implications not only for the stability of lanthanides co-precipitated with calcite but possibly also for trivalent actinides. Because the ionic radii of Am^{3+} and Cm^{3+} are similar to those of Nd^{3+} and Sm^{3+} (and larger than those of Dy^{3+} and Yb^{3+}), we speculate that Am^{3+} and Cm^{3+} are also likely to be incorporated in calcite with significant disruption of the local environment, making these phases more susceptible to dissolution, and allowing remobilization of the radionuclides.

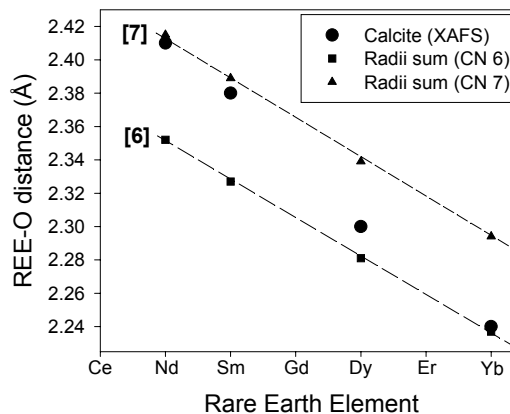


Fig. 5. Comparison of first-shell REE-O distances from EXAFS data for Nd-, Sm-, Dy-, and Yb-doped calcite with model distances based on ionic radii for 6-fold and 7-fold coordination with oxygen. (Elzinga et al., 2002).

We also performed optical spectroscopy on Nd^{3+} -containing calcite to determine the uniqueness of the local defect coordination (i.e., if the local environment is the same for all Nd atoms in the sample). The optical spectroscopy showed a broad distribution of crystal field environments for the Nd^{3+} in calcite, providing evidence for inhomogeneous strain associated with a range of defect structures (Withers et al., 2003). We were not able to determine whether (or how) charge-compensation played a role in producing the local distortions.

We also performed experiments in solutions pre-equilibrated with calcite to examine the adsorption behavior of Sm^{3+} and Yb^{3+} on calcite. Using initial Sm^{3+} or Yb^{3+} concentrations of 1–5 μM we find that precipitation or surface precipitation occurs for both species. EXAFS spectra suggest that the phases show some resemblance to lanthanide carbonate hydrates, but their identities remain unknown. This finding may be significant in assessing clean-up methodologies. When no active calcite crystallization is occurring, the lanthanide species are sequestered as separate phases. Such second phases could be more readily dissolved depending on their solubilities, which remain unknown. Similar behavior may occur for trivalent actinides.

The results of our work on lanthanide uptake by calcium carbonate are presented in two papers (Elzinga et al., 2002; Withers et al., 2003). Vibrational spectroscopy of Nd-doped calcite represented a portion of the PhD thesis research of Sandra Withers. An additional paper describing results of lanthanide adsorption is expected to be submitted for publication within several months.

Pb²⁺ Uptake by Calcite and Comparison with Uptake of other Divalent Heavy Metals

One of the major focus areas of our work addressed the systematics and mechanisms of Pb²⁺ uptake by calcite under conditions relevant to surface contamination. A contaminant species with serious health risks, Pb²⁺ is also important owing to its high affinity for sorption on oxide, hydroxide, and carbonate surfaces. However, Pb²⁺ also forms stable complexes with dissolved CO₃²⁻, raising the potential for competition between surface-bound and aqueous carbonate. We employed multiple, complementary approaches for quantifying Pb²⁺ sorption and co-precipitation with calcite, examining the effects of various system parameters so that results would be broadly applicable. This work included batch experiments to establish sorption isotherms and the kinetics of sorption as a function of Pb concentration, solid/solution ratio, ionic strength, background electrolyte type, and solution pH (Rouff et al., 2003a). Desorption experiments were conducted to assess the reversibility of sorption over time. Use of Pb-210 radiotracer combined with gamma spectroscopy allowed high precision measurements of Pb partitioning behavior. The calcite sorbent was carefully pre-equilibrated to make the conditions relevant. Calcite that has not been pre-equilibrated is unusually reactive, undergoing dissolution and precipitation; consequently, unintended metal uptake may occur that is not necessarily representative of processes occurring in nature.

Parallel experiments were conducted to assess Pb²⁺ co-precipitation behavior with calcite. Our results show that Pb²⁺ is strongly partitioned into calcite during growth, with co-precipitation K_d values exceeding 100 for the experimental conditions employed. This finding is significant for DOE clean-up strategies because co-precipitation is now recognized to be a dominant mechanism of metal uptake by calcite. Hence natural calcite precipitation or the use of metastable forms of calcium carbonate (e.g., aragonite) in permeable reactive barriers should be highly effective in removing Pb from soil and ground waters.

The results obtained from these studies provide new information that can benefit DOE's clean-up efforts and potentially offer new methodologies for selective uptake of heavy metals complexed by carbonate species. Both the isotherms and kinetic experiments quantitatively demonstrate that calcite has a very high affinity for sorbing dissolved lead over a broad range of solution conditions. Consequently, calcite, whether occurring naturally or in an engineered permeable reactive barrier, should be a highly effective sorbent for Pb²⁺. K_d values (for adsorption) for our experimental conditions are in the range of 1000–2000 mL/g. Although, such K_d values have been widely used to predict contaminant partitioning in first-generation reactive-transport models, the variation in sorption behavior with solution conditions makes them less attractive for more sophisticated modeling. Our results also provide a quantitative basis for surface complexation models of Pb sorption on calcite.

The results of kinetic studies indicate two uptake processes for initial Pb concentrations below saturation with respect to cerussite (PbCO₃) and hydrocerussite. (At higher Pb concentrations surface precipitation is evident.) The rapid uptake process is nearly complete within 24 hr, but a slower uptake process was observed to occur for periods exceeding hundreds of hours. A slow but long duration uptake mechanism is potentially important for predicting the uptake and mobility of dissolved Pb. Contamination events generally result in interaction periods that greatly exceed the duration of laboratory experiments. Hence actual uptake in field setting may greatly exceed predictions based on short-term experiments.

Our EXAFS spectroscopic characterization of the Pb speciation at the calcite-water interface shows that the rapidly sorbed Pb is bound as an inner-sphere surface complex with three or four oxygen ligands (Rouff et al., 2003b). The Pb-O distance (2.34 Å) and oxygen coordination number (3–4) are consistent with a trigonal pyramidal or square pyramidal surface complex, which is markedly different from its coordination as a dopant in the calcite structure, where EXAFS studies have shown it to substitute in the Ca site in octahedral coordination with a Pb-O distance of 2.52 Å (Reeder et al., 1999). This difference is evident in radial structure functions comparing Pb²⁺ co-precipitated with calcite and Pb²⁺ adsorbed on calcite (Fig. 6). Bargar et al. (1997) examined Pb²⁺ sorption complexes on alumina using EXAFS and found first-shell Pb-O distances ranging from 2.20–2.32 Å, which are roughly similar to our values for Pb²⁺ adsorption on calcite. We note that our result for Pb²⁺ adsorption differ from the observations made by Sturchio et al. (1997) for Pb-EDTA interaction at the calcite surface. Using X-ray standing wave and reflectivity methods (*ex situ*), these authors observed a position for Pb corresponding to exchange in a surface Ca site. This different result may reflect the procedure used for introducing Pb and subsequent interactions at the calcite surface.

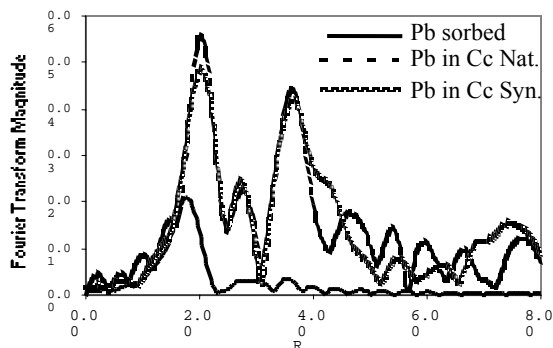


Fig. 6. Radial structure functions from EXAFS spectra of Pb²⁺ sorbed on calcite and two samples of Pb²⁺ co-precipitated with calcite. (Rouff et al., 2003b)

Over the duration of our experiments, there was insufficient uptake of Pb by the slower process to distinguish it from rapidly sorbed Pb using EXAFS (which averages over all Pb atoms in the beam path). Our desorption experiments showed that 80–90% of the Pb sorption is reversible, but 10–20% is retained over time scales of 60 hr. We speculate that the retained Pb has co-precipitated in surface layers of the calcite. Identifying the mechanism of uptake for this slower kinetic process should be an important research goal for future studies.

Experiments assessing the pH dependence of Pb²⁺ sorption exhibit a sorption maximum at pH 8.4–8.5. This maximum corresponds very closely to dominance of the aqueous speciation by the neutral PbCO₃⁰ species (Fig. 7) in our calcite-equilibrated solutions. At lower pH, where the free Pb²⁺ species becomes dominant, sorption decreases. We believe this result has potentially important implications for predicting sorption behaviors of other metal carbonate complexes (including those of radionuclides) by calcite and other carbonates. For some metals, formation of carbonate complexes decreases sorption by stabilizing the aqueous complex. Our results show that the neutral PbCO₃⁰ species is favored for adsorption at the calcite surface, and our EXAFS results document the formation of an inner-sphere surface complex. Consequently, surface-bound CO₃ ligands compete favorably with aqueous CO₃²⁻ ligands for Pb²⁺. This suggests the likelihood that carbonate complexes of other divalent and trivalent metals may exhibit strong uptake onto calcite.

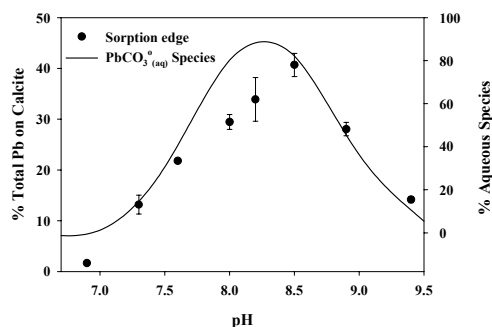


Fig. 7. Pb sorption maximum as a function of pH (circles). Percentage of total Pb as the PbCO₃⁰ species as a function of pH (solid line; right scale).

For DOE cleanup efforts, this has the greatest relevance for trivalent actinides, such as Am^{3+} , which forms stable carbonate complexes.

Previous studies have demonstrated that divalent transition metals also sorb strongly at the calcite surface (e.g., Zachara et al., 1991). In view of our findings of non-octahedral coordination of Pb^{2+} sorbed at the calcite-water interface, we carried out in situ EXAFS spectroscopic studies to characterize the structure of Zn^{2+} and Cu^{2+} sorption complexes on calcite (Elzinga and Reeder, 2002). Zn^{2+} was found to form an inner-sphere tetrahedral surface complex, which differs from the octahedral coordination for Zn^{2+} incorporated into calcite. Cu^{2+} coordination is generally found to be affected by a Jahn-Teller distortion, resulting most commonly in an axially distorted octahedral complex. We found this to be true for Cu^{2+} adsorbed at the calcite surface as well as Cu^{2+} incorporated into bulk calcite. However, subtle differences in the axial oxygens distinguish these different states for Cu^{2+} . Taken together, our results indicate that sorption complexes of strongly binding metals at the calcite-water interface are commonly different in configuration than the same metal incorporated into the bulk calcite. This observation is important for formulation of accurate predictive models of contaminant sequestration. The high affinity of these divalent metals species for the calcite surface may result from the preference for specific coordination at the surface. The formation of such inner-sphere complexes may also be associated the observed slow uptake of metals over longer time periods.

Results on Pb^{2+} sorption represents a portion of the PhD thesis of A. Rouff; two papers are in review (Rouff et al., 2003a, 2003b), and one other papers will be submitted shortly. Results for Zn^{2+} and Cu^{2+} uptake by calcite are presented in a paper by Elzinga and Reeder (2002).

Cs^+ Sorption on Calcite

Cs^+ is present in the Hanford subsurface and poses a serious remediation problem. Cs^+ , an important radionuclide species, commonly exhibits a low affinity for sorption with a number of common mineral surfaces and consequently can have a high mobility in the soil, vadose, and phreatic zones. Few studies have examined Cs^+ sorption by calcium carbonate minerals, and no comprehensive dataset is available for calcite. In view of the common and varied occurrence of calcite in Hanford sediments, one component of our research addressed Cs^+ sorption on calcite. Although limited in overall scope, our research efforts sought to provide a quantitative basis for evaluating the potential for Cs^+ adsorption on calcite over the pH range 7.5–8.5 and for a range of ionic strength and solid/solution conditions. Batch sorption experiments used Cs-137 radiotracer to allow for precise measurements of Cs^+ partitioning. Our results for Cs adsorption conducted for durations up to 200 hr confirmed a very weak interaction with the calcite surface ($K_d \sim 1$ mL/g). This was not significantly influenced by ionic strength or solution pH. Desorption experiments demonstrated that Cs^+ adsorption was almost completely reversible. This confirms that calcite should play little role in sequestration of Cs^+ . This behavior contrasts sharply with the uptake behaviors of Pb^{2+} and lanthanide species. Our confirmation of little sorption capacity of calcite for Cs^+ provides valuable, if disappointing, data for reactive transport codes used for prediction or verification models. Work on Cs^+ adsorption represents part of the PhD thesis of graduate student A. Rouff.

Chromate (CrO_4^{2-}) Uptake by Calcite

Cr(VI) , occurring as the tetrahedral CrO_4^{2-} anion, is highly mobile and poses a risk in the subsurface at Hanford and at other sites in the DOE Complex. CrO_4^{2-} also commonly exhibits only a very weak tendency for interaction with minerals, thereby limiting its uptake. Previous

studies with sulfate, also a tetrahedral oxyanion (SO_4^{2-}), showed that coprecipitation with calcite was significantly enhanced by rapid crystallization (Busenberg and Plummer, 1985), as might occur during evaporation or induced precipitation. We examined the coprecipitation of CrO_4^{2-} with calcite under conditions of high ionic strength. Because of the steric incompatibility of a tetrahedral complex substituting in calcite, we focused on the mechanism of such a substitution to determine if defect substitution could occur. We coprecipitated CrO_4^{2-} with calcite over a range of total CrO_4^{2-} concentrations. As suspected, CrO_4^{2-} is highly incompatible with calcite, as demonstrated by K_d values (for co-precipitation) less than one. By forcing rapid crystallization, however, we obtained calcite containing hundreds of ppm Cr. EXAFS and XANES spectroscopy were used for characterization of the incorporated Cr. The most striking finding was that the distinct pre-edge feature indicative of Cr(VI) was significantly reduced relative to known Cr(VI) standards. This indicates that some of the Cr(VI) was reduced to Cr(III) during the coprecipitation. This was confirmed by modeling the XANES using linear combinations of Cr(VI) and Cr(III) XANES spectra from standards. We are currently investigating the possible causes of this unexpected behavior. Some workers have reported that Cr(VI) may be reduced to Cr(III) in the intense X-ray beam available at synchrotrons. We are testing this and other possibilities now and expect to have further insight to the role of coprecipitation with calcite for attenuating CrO_4^{2-} mobility within the next several months.

Sr²⁺, Co²⁺, and Pb²⁺ Interaction with Natural Caliche Samples

Natural materials occurring in the soils and vadose zone are typically heterogeneous, offering multiple sites for uptake and interaction. We examined the interactions of Sr²⁺ and Pb²⁺ with naturally occurring caliche from near the Hanford Site and having similar characteristics to assess the importance of surface reaction sites. Different approaches were explored to evaluate the dominant interaction types. In batch experiments, caliche fragments were exposed to Co²⁺ and Pb²⁺ containing solutions over a range of pH and solution chemistries. Samples were then dried or briefly rinsed and dried to simulate intermittent wetting/drying that might occur in the vadose zone. The caliche fragment surfaces and cross-sections were characterized by spatially resolved micro X-ray fluorescence and micro-XANES. Both Co and Pb were found to be heterogeneously distributed on the caliche fragments. In both cases, the metals were associated with the calcium carbonate dominant portions of the sample, as opposed to secondary phases that invariably exist in natural caliche. The highly localized nature of the metal suggested surface precipitation. Depending on solution chemistry, the precipitate was either a chloride and a hydroxide, indicating that non-carbonate precipitates may be significant for metal interactions with caliche.

For the studies involving Sr, the caliche was found to contain significant Sr acquired during pedogenesis. The Sr distribution was mapped using micro-XRF, showing a nearly identical distribution with the Ca. This suggests that Sr was simply co-precipitated with the calcite during pedogenesis.

The results of these studies were presented as a poster at the 10th Advanced Photon Source User's Meeting May, 2000 (Beck et al., 2000).

Collaborations Formed During the Previous Research Program

Over the course of our research activities, we found it beneficial to forge collaborations with scientists having particular expertise. There was considerable interaction with Drs. C. Drew Tait and David E. Morris at Los Alamos National Lab, involving actinide geochemistry. This collaboration began within the first year of the award and proved particularly important for characterization of the uranyl species using luminescence spectroscopy, including decay kinetics, and vibrational spectroscopy. We also benefited by directly involving experienced optical

spectroscopists in the Department of Physics at the University of Central Florida (Dr. Robert E. Peale and graduate student Sandra Withers). It was largely through this collaboration that we were able to characterize the local coordination of Nd^{3+} in calcite. Much of our experiment effort required access to synchrotron beamlines and the experience of scientists who specialize in their applications. By working closely with Dr. Steve Heald (EMSL-PNNL) at the PNC-CAT beamline at the Advanced Photon Source we were able to obtain and interpret micro-XAS data as well as EXAFS spectra on a variety of U-containing and Cr-containing samples. Similarly, Dr. Lynne Soderholm (Argonne National Lab) worked with us on EXAFS experiments involving radionuclides at the Advanced Photon Source.

Post-doctoral and Graduate Student Involvement

Much of the research was carried out by graduate students and post-docs under the direction of the P.I. and co-P.I.s. One post-doc and five graduate students participated in this research program. Two PhD theses are centered on topics described above; one has been completed and the other will be completed within roughly one year.

Papers Cited and Papers Resulting from DOE Award (*)

- Bargar J.R., Brown Jr G.E., and Parks G.A. (1997) Surface complexation of Pb(II) at oxide-water interfaces: I. XAFS and bond-valence determination of mononuclear and polynuclear Pb(II) sorption products on aluminum oxides. *Geochim. Cosmochim. Acta* 61, 2617-2637.
- *Beck, K.M., Hess, W.P., Heald, S.M., Withers, S.H., Peale, R.E., and Reeder, R.J. (2000) Strontium migration and co-precipitation at Columbia Basin basalt/caliche interfacial regions. *Advanced Photo Source Annual Mtg.*
- Busenberg E. and Plummer L.N. (1985) Kinetic and thermodynamic factors controlling the distribution of SO_4^{2-} and Na^+ in calcites and aragonites. *Geochim. Cosmochim. Acta* 49, 713-725.
- *Elzinga, E.J., Reeder, R.J., Withers, S.H., Peale, R.E., Mason, R.A., Beck, K.M., and Hess, W.P. (2002) EXAFS study of rare-earth element coordination in calcite. *Geochim. Cosmochim. Acta*, 66, 2875-2885.
- *Elzinga, E.J. and Reeder, R.J. (2002) X-ray absorption spectroscopy study of Cu^{2+} and Zn^{2+} adsorption complexes at the calcite surface: Implications for site-specific metal incorporation preferences during calcite crystal growth. *Geochim. Cosmochim. Acta*, 66, 3943-3954.
- *Elzinga, E.J., Tait, C.D., Reeder, R.J., Rector, K.D., Donohoe, R.J., and Morris, D.E. (2003) Spectroscopic study of U(VI) sorption at the calcite-water interface. *Geochim. Cosmochim. Acta*, (in review)
- Lee, Y.J., Reeder, R.J., Wenskus, R.W., and Elzinga, E.J. (2002) Structural relaxation in the MnCO_3 - CaCO_3 solid solution: a Mn *K*-edge EXAFS study. *Phys. Chem. Minerals*, 29, 585-594.
- Pabalan R.T., Turner, D.R., Bertetti F.P., and Prikryl J.D. (1998) Uranium^{VI} sorption onto selected mineral surfaces. In E. Jenne (ed.), *Adsorption of Metals by Geomedia*, 99-130, Academic Press, San Diego, California.
- Paquette J. and Reeder R.J. (1995) Relationship between surface structure, growth mechanism, and trace element incorporation in calcite. *Geochim. Cosmochim. Acta* 59, 735-749
- Payne T.E., Lumpkin G.R., and Waite T.D. (1998) Uranium^{VI} adsorption on model minerals. In E. Jenne (ed.), *Adsorption of Metals by Geomedia*, 75-97, Academic Press, San Diego, California.
- *Rakovan, J., Reeder, R.J., Elzinga, E.J., Cherniak, D.J., Tait, C.D., and Morris, D.E. (2002) Characterization of U(VI) in the apatite structure by X-ray absorption spectroscopy. *Env. Sci. Tech.*, 36, 3114-3117.
- Reeder R.J. (1996) Interaction of divalent cobalt, zinc, cadmium, and barium with the calcite surface during layer growth. *Geochim. Cosmochim. Acta* 60, 1543-1552.

- Reeder, R.J., Lamble, G.M., Northrup, P.A. (1999) XAFS study of the coordination and local relaxation around Co^{2+} , Zn^{2+} , Pb^{2+} , and Ba^{2+} trace elements in calcite. *Am. Mineral.*, 84, 1049-1060.
- *Reeder R.J., Nugent M., Lamble G.M., Tait C.D., and Morris D.E. (2000) Uranyl incorporation into calcite and aragonite: XAFS and luminescence studies. *Environ. Sci. Technol.* 34, 638-644.
- *Reeder, R.J., Nugent, M., Tait, C.D., Morris, D.E., Heald, S.M., Beck, K.M., Hess, W.P., and Lanzirrotti, A. (2001) Coprecipitation of uranium(VI) with calcite: XAFS, micro-XAS, and luminescence characterization. *Geochim. Cosmochim. Acta*, 65, 3491-3503.
- Reeder, R.J., Nugent, M. and Pabalan, R.T. (2001) Local structure of uranium(VI) sorbed on clinoptilolite and montmorillonite. In: Cidu, R. (ed.), *Water-Rock Interaction*, A.A. Balkema Publishers, Lisse, The Netherlands, 423-426.
- *Rouff A.A., Reeder R.J., and Fisher N.S. (2003a) Pb(II) sorption with calcite: A radiotracer study. *Aquatic Geochem.* (in review)
- *Rouff A.A., Elzinga E.J., Reeder R.J. and Fisher N.S. (2003b) EXAFS evidence for the formation of Pb(II) inner-sphere complexes and precipitates on calcite. *Environ. Sci. Technol.* (in review)
- Sturchio N.C., Chiarello R.P., Cheng L., Lyman P.F., Bedzyk M.J. and Baer D.R. (1997) Lead adsorption at the calcite-water interface: Synchrotron X-ray standing wave and X-ray reflectivity studies. *Geochim. Cosmochim. Acta* 61, 251-263.
- *Withers, S.H., Braunstein, G., Peale, R.E., Beck, K.M., Hess, W.P., and Reeder, R.J. (2003) Broad distribution of crystal field environments for Nd^{3+} in calcite. *Phys. Chem. Minerals* (accepted for publication)
- Zachara J.M., Cowan C.E. and Resch C.T. (1991) Sorption of divalent metals on calcite. *Geochim. Cosmochim. Acta* 55, 1549-1562.