

FINAL REPORT: “Coupling Sorption to Soil Weathering During Reactive Transport: Impacts of Mineral Transformation and Sorbent Aging on Contaminant Speciation and Mobility” (DE-FG02-06ER64192, 2/15/06-1/31/09). *Principal Investigators:* Jon Chorover (University of Arizona [UA]), Karl Mueller (Pennsylvania State University [PSU]), Peggy O’Day (University of California, Merced [UCM]), R. Jeff Serne (Pacific Northwest National Laboratory [PNNL]), and Carl Steefel (Lawrence Berkeley National Laboratory [LBNL]). Project personnel also includes postdoctoral associates Sunkyung Choi (UCM), Aaron Thompson (UA) and Wooyong Um (PNNL), Ph.D. students Nelson Rivera (UCM) and Caleb Strepka (PSU), and research specialist Mary Kay Amistadi (UA).

The goal of our project is a predictive-mechanistic understanding of the coupling between mineral weathering and contaminant (Cs, Sr, I) fate in caustic waste-impacted sediments at the Hanford Site. Through bench-scale experiments, we have identified geochemical transformations that alter the mobility of priority pollutants (Cs, Sr, I) in subsurface environments characteristic of high-level radioactive waste (HLRW)-impacted DoE sites. Our studies are designed to model the unique chemistry of this subsurface contamination, to quantify rates of contaminant uptake and release, and to identify molecular mechanisms of time-dependent, irreversible sequestration of contaminants into the solid phase. Our approach is to link quantitative macroscopic measures of contaminant mobility and partitioning to the molecular-scale mechanisms that mediate them. We have found that the molecular mechanisms themselves change with time and system composition in response to the evolving chemistry of contaminant-solution-mineral interactions. Specifically, our results show that contaminant fate is closely coupled to the major silicate incongruent weathering reactions that occur when soil solids are contacted with aqueous solutions under conditions that are far from equilibrium. Neoformed precipitates - including carbonate, feldspathoid and zeolite phases, have been observed to sequester Cs and Sr under caustic waste conditions. In contrast, iodide is less effectively sequestered into the neoformed precipitates. In any case, the long-term stability of these co-precipitates must be assessed, particularly in respect to the site closure scenario wherein sediment pore water is expected to return to a “natural” pH and ionic strength fed by rainwater recharge after removal of the caustic source.

Our research centers on a series of saturated and unsaturated column studies conducted on Hanford Formation sediments that had been previously reacted in batch or column systems with synthetic tank waste leachate (STWL) for up to 1 year in the presence and absence of CO₂. Batch or column STWL-reacted sediments are then subjected to column leaching experiments using simulated background pore water (BPW) solution to assess subsequent contaminant release. We used a multi-faceted approach (XAS, XRD, DRIFT, NMR, TEM/EDS, wet chemistry) to investigate molecular-scale mechanisms that give rise to macroscale response. In order to develop efficient predictive tools applicable to the Hanford site our work involves (1) production of laboratory-weathered sediments under conditions representative of caustic waste release; (2) mineralogical characterization and contaminant molecular speciation of the STWL-weathered (time = 0) sediments; (3) intensive monitoring of element release trajectories during controlled BPW infiltration; (4) mineralogical characterization and contaminant molecular speciation of BPW-leached (time = final) sediments; use of (2) through (4) to constrain mechanistic reactive transport modeling of contaminant release from weathered sediments.

Batch and Column STWL reactions. Hanford sediments were reacted in the presence of two hyperalkaline waste simulants and two CO₂ partial pressures. These simulants contained either “high” or “low” levels of Cs, Sr and I contamination and the weathering reactions took place under either atmospheric- or CO₂-free conditions. In all treatments, added Sr, Cs and I were incorporated into the solid phase with 3 to 12 times more uptake of Sr than Cs, and much smaller uptake of I. Sediment CEC and specific surface area decreased with STWL reaction time, consistent with the dissolution of clay minerals. But a finer granulometry was also observed, consistent with the neoformation of fine-grained particles. XRD, DRIFT and microscopic characterizations indicated the precipitation of Ca/Na-rich zeolites for the highest contaminant concentrations (HIGH: 10⁻³ m Cs and Sr, 10⁻⁵ m I) and NO₃-feldspathoids

(sodalite/cancrinite-like) for the low concentrations (LOW: 10^{-5} m Cs and Sr, 10^{-7} m I) with detectable amounts of Sr and Cs in the neophases for HIGH. Iodine uptake could not be localized in the solid phase. Intensities of neophase XRD reflections increased with reaction time. Moreover, the extent of calcite dissolution decreased with increasing PCO_2 , and the accompanying Ca^{2+} release resulted in the production of a stratlingite-type phase.

Homogenous nucleation experiments conducted under similar conditions revealed the precipitation of similar neophases with a step-wise mineral transformation from zeolite to feldspathoid occurring between 30 and 365 d in both HIGH and LOW. Therefore, assuming similar neophases in sediments and given the presence of zeolite in HIGH after 1 y, mineral transformation (i.e., ripening) appears to be inhibited for HIGH sediment treatments. Linear combination fitting of Sr K-edge EXAFS of the weathered sediments and homogenous nucleation products showed Sr sequestration into sodalite-type sites in the LOW treatment, whereas Sr siting in the HIGH was dependent on PCO_2 . Strontium was incorporated into chabazite-type minerals in CO_2 -free conditions, whereas it was sequestered into sodalite-type and strontianite phases when CO_2 was present at atmospheric levels.

Flow-through columns of Hanford sediment were also subjected to STWL infusion. In this case, sediment was reacted with a “HIGH” STWL solution containing 10^{-3} m Cs and Sr. Reactant STWL was flushed through the column until breakthrough, and then flow was stopped, allowing the solution to react for 1 day to 3 months. Sr-EXAFS of the first 0-13 mm and 52-76 mm of the column, show Sr in sodalite-like and chabazite-like sites, superimposed with native (i.e., feldspar-like) strontium coordination. With increased sediment aging, the signal from the unreacted sediment decreases and a greater contribution is derived from neoformed phases. Although, no Cs EXAFS spectra were collected, NMR data indicates Cs is incorporated into both the neoformed phases and clay edge sites

^{27}Al and ^{29}Si NMR Studies of Reacted Sediments. Solid-state NMR experiments are being performed on the batch-reacted Hanford sediments. High-field silicon-29 and aluminum-27 magic-angle spinning (MAS) NMR experiments are completed or in progress, and cesium-133 MAS studies are planned in our follow-on award.

Reacted Hanford sediment samples contain a range of clays, phyllosilicates and other silica/alumina species that are detectable through the use of solid-state NMR. The presence of this variety of components results in slight NMR shift changes that yield broad spectra, presenting a challenge to simple interpretation. Enhanced MAS NMR methods (i.e., faster sample rotation) have rendered the resulting spectra easier to interpret: removing overlapping sidebands that arise from parent material with octahedral aluminum coordination, and which occlude the more interesting resonances from tetrahedrally-coordinated aluminum, will allow more concrete phase assignments.

In anticipation of exploring weathered Hanford sediments containing neophases comprised of zeolite and/or feldspathoid materials, we also have begun a study of strontium-87 NMR of Sr-exchanged zeolite samples. These spectra are obtained under conditions of magic-angle spinning while also utilizing the Quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) pulse sequence. In addition, and since strontium and calcium carbonate phases are important in the time-evolution of the weathering products in our team's experiments, we have initiated a study of co-precipitated Sr/Ca carbonates, and have acquired a series of static strontium-87 QCPMG spectra for pure strontium carbonate as well as co-precipitate samples with Sr/Ca ratios ranging from 0.01 to 16. We are currently analyzing this large set of data with the intention of fitting a series of models of Sr/Ca ordering, and simultaneously beginning computational chemistry calculations of strontium-87 NMR parameters (isotropic chemical shift and quadrupolar parameters) to aid in modeling these data.

Sr-EXAFS Results for Batch Experiments. All three natural sediments contained native Sr in concentrations that are measurable by EXAFS (HC = 420 ppm; HF = 340 ppm; RG = 170 ppm). For short equilibration times (1-7 d), native Sr represents a significant fraction of total Sr in the bulk sample since Sr taken up from reactant solutions is between 746-1955 ppm. Thus, the native Sr fraction must be accounted for in the spectra of 7 d reacted samples and 30 d samples extracted with AAO. Quantitative analyses of Sr-EXAFS of unreacted sediments indicate two primary Si/Al distances around Sr in the unreacted sediment (at 3.35 and 3.81 Å), consistent with Sr in the Ca site of plagioclase feldspar. For batch-reacted sediments at 7 d and 33 d, bulk EXAFS spectra (not shown) indicate that Sr from reaction with STWL is incorporated mostly into poorly crystalline, neoformed aluminosilicates, rather than precipitated as $\text{SrCO}_3(\text{s})$, as seen in the kaolinite system. Backscattering from neoformed phases is overprinted on the Si/Al scattering in the native Sr-bearing phases, which all have second-neighbor Si/Al atoms within a similar range (~ 3.35 and 3.81 Å). However, constraining interatomic distances from analysis of the unreacted sediments and fitting the remaining spectral features indicates additional Si/Al scattering at slightly different interatomic distances that give rise to cancellation of scattering amplitude.

After one year of reaction, the mass of added Sr incorporated in the solid phase (> 1000 ppm) is much greater than native Sr and thus, the native Sr component was not included in the EXAFS fits. In HC and HF sediments, a fraction of Sr is associated with $\text{SrCO}_3(\text{s})$ (data not shown). This result is similar to that found in the model clay systems reacted under the same conditions, which show mixtures of $\text{SrCO}_3(\text{s})$ and neoformed aluminosilicate phases. For illite, $\text{SrCO}_3(\text{s})$ dominates the EXAFS spectrum, but montmorillonite and vermiculite have different proportions of $\text{SrCO}_3(\text{s})$ and aluminosilicate neophases. Although $\text{SrCO}_3(\text{s})$ has a strong spectral signature, it is not the major Sr component in the reacted sediment samples. The $\text{SrCO}_3(\text{s})$ fraction is easily removed by chemical extraction, as shown by EXAFS analyses of AAO-extracted samples in which no $\text{SrCO}_3(\text{s})$ is present. The extraction results indicated that 114 ppm and 1163 ppm Sr for one-year HC and HF, respectively, is removed by AAO, placing an upper limit on the amount of Sr associated with $\text{SrCO}_3(\text{s})$ at $\sim 3\%$ (for HC) and $\sim 30\%$ (for HF) of the total Sr.

In both reacted sediments and model clays, the majority of Sr is associated with neoformed feldspathoid phases after one year, which is best seen in the AAO-extracted samples. The lack of prominent second-neighbor backscattering in the one-year samples compared to unreacted sediments and short-term reacted samples is probably a result of cancellation of scattering paths from Sr bonded in multiple neophases. Bulk XRD, FTIR, and SEM/EDS characterizations confirmed the presence of secondary sodalite and cancrinite, in addition to other unidentified zeolite-type phases, associated with Sr and Cs after 182 d to one year of reaction, and synchrotron microfocused X-ray diffraction data showed Sr was associated with these neoformed solids. Element mapping with synchrotron micro-XRF shows a strong correlation between Sr and Ca in some sediment particles but not in others, and likewise no consistent correlation between Sr and Fe (Fig. 2). These results are consistent with irreversible Sr incorporation into neoformed feldspathoid-type phases, but also show that excess Sr not associated with these phases readily precipitates as $\text{SrCO}_3(\text{s})$.

Contaminant release by background pore water (BPW) leaching. In order to assess contaminant release upon neutral solution infiltration, all types of artificially weathered materials (sediments in batch reactors, stop-flow column weathered sediments and homogenous nucleation products) were leached with simulated BPW (pH=7) in flow-through saturated and unsaturated columns.

Leaching studies of batch weathered sediments: When the batch reacted sediments were leached with simulated BPW (pH=7) in flow-through saturated and unsaturated columns, major cation release and pH stabilized at pore volume (PV) > 300 . Long term fractional release of Sr and Cs in all treatments was very low. Conversely, rapid I desorption was observed, with the total sorbed pool diminished by ca. 50% in within 50 PV. Dissolution of solid phases, assessed by XRD after 600 PV, indicated persistence of NO_3 -feldspathoids in the LOW and incongruent zeolite dissolution in the HIGH.

Sediment column experiments: After various reaction times (1 day to 3 months), the flow-through weathered sediments were immediately flushed with BPW. Effluent Cs and Sr were measured and normalized to the total amount loaded during reaction with STWL and, for Sr, included native Sr present in the sediment. Strontium exhibits greater retention over Cs during contaminant uptake, with Cs showing breakthrough two times faster than Sr. During flush out with BPW, initial Cs release is rapid and reaches a steady state after ~10 PV. Depending on stopped-flow reaction time, 10-25% of total sorbed Cs is eluted after 500 PV. Strontium desorption is retarded until 25-50 PV. However, Sr exhibits a more rapid release than Cs after the initial retardation and up to 55% total Sr (sorbed and native in sediment minerals) is eluted from the column after 500 PV. The desorption behavior is consistent with rapid desorption of Cs associated with exchange sites, followed by a steady-state release. Longer reaction and aging times lead to the formation of recalcitrant phases that sequester Sr and Cs and are resistant to desorption. The pH takes approximately 200 PV to reach a steady state value of ~8.3. The effluent pH never reached the influent value of 7 during the course of the experiment. Ca and Mg release are both retarded with calcium breaking through at 50 PV and magnesium at 150 PV. Na and K show a similar trend with sodium reaching breakthrough at ~50 PV and K at 100 PV. No Al or Si was added to the initial BPW. The Si has a higher effluent concentration than Al by a factor of 10.

Reactive transport modeling of contaminant release. Based on the characterization of the STWL-weathered sediments, the BPW-leached sediments and the elemental release monitoring upon BPW infiltration, hypotheses governing the short-term and long-term release of contaminants have been formulated. Specifically, we postulate that Sr and Cs releases are governed by neoprecipitate dissolution as well as by ion-exchange processes. In order to test these hypotheses, the evolution of STWL-weathered sediment infiltrated by BPW had been numerically modeled using the reactive transport model CRUNCHFLOW. This model takes into account both mineral dissolution and ion-exchange in complex systems.

Short term release of contaminants: The leaching behavior and release mechanism of Sr and Cs from unsaturated columns packed with batch weathered Hanford sediment (atmospheric PCO_2) has been studied with CRUNCHFLOW. In summary of the short-term modeling of the unsaturated column leaching experiments, the simulated result shows a reasonable match with experimental data, validating fundamental assumptions. The early release of both Sr and Cs appears mostly derived from dissolution of amorphous zeolite containing contaminants (chabazite-type mineral). Sorption and/or precipitation are considered as the dominant mechanisms that remove contaminants from solution after the early release of Sr and Cs. Identification and quantification of amorphous zeolite, which is unstable in the early stage, are critical to better understand of the mechanisms of released contaminants in both short-term and long-term modeling. The occurrence of other possible mechanisms needs to be considered in the early stage. The release of Sr is mostly controlled by mineral dissolution and precipitation in HIGH[CO_2 +] column, whereas ion exchange processes appear more important in the LOW[CO_2 +]. The abrupt release of Sr in the latter period of the leaching experiment of HIGH[CO_2 +] indicates the dissolution of another type of more crystalline mineral (e.g., cancrinite) containing Sr. One active site ion exchange process successfully simulates the overall behavior of released Cs in LOW[CO_2 +] column. However, two active sites model is needed to describe the additional release of Cs in the latter period of the experiment with HIGH[CO_2 +] sediment.

Long term release of contaminants: Numerical modeling of the long-term release of Cs and Sr could be achieved in the LOW, whereas the presence of zeolite in the HIGH makes the modeling more complex. According to the available thermodynamic data, feldspathoids that precipitate after contact of Hanford sediments with hyperalkaline waste are likely to dissolve upon introduction of BPW because undersaturation of solution with respect to these phases is maintained in the effluent through leaching. In contrast, the effluents of all treatments are always slightly oversaturated with respect to both gibbsite and

kaolinite, whereas they are undersaturated with respect to calcite and strontianite. Those assumptions were used as initial condition of simulation. Cs effluent behavior between 300 and 600 PV's can be explained solely by release via ion exchange on frayed edge sites (FES); there is no need to evoke a mineral dissolution source to explain Cs effluent concentrations. Cs is partitioned almost entirely to the FES, and release is governed primarily by K^+ exchange. Sr release behavior is well approximated by dissolution of neoformed feldspathoids substituted with Sr. Due to the unexpected importance of chabazite, modeling of the HIGH treatments is under development.

Publications

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