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*Project Title: **Caustic Waste-Soil Weathering Reactions and Their Impacts on Trace Contaminant Migration and Sequestration***

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High pH waste solutions are in gross chemical disequilibrium with the subsurface environment and react with sediment minerals, promoting dissolution and precipitation processes that impact ^{137}Cs , ^{90}Sr , and ^{129}I speciation and migration behavior in the vadose zone. We have conducted long-term kinetic studies, with reaction times ranging from 1 to 369 d, to examine relationships between aluminosilicate weathering in the presence of synthetic tank waste leachate (STWL) and contaminant uptake and release. Our experiments employ a sequence of specimen clay minerals including illite, vermiculite, montmorillonite and kaolinite, which are also important reactive solids in the Hanford sediments. These studies have shown direct coupling between mineral transformation reactions and contaminant sequestration/stabilization.

The main objectives of the current project are to (1) measure the coupling of clay mineral weathering and contaminant uptake kinetics over an expanded range in aqueous geochemistry and soil moisture content (saturation) representing a gradient from near-field to far-field conditions; (2) determine the molecular structure of contaminant binding sites and their change with weathering time during and after exposure to STWL; (3) establish the stability of neoformed weathering products and their sequestered contaminants upon exposure of the solids to more "natural" soil solutions (i.e., after removal of the caustic waste source); and (4) integrate macroscopic, microscopic and spectroscopic data to distinguish labile from non-labile contaminant binding environments, including their dependence on system composition and weathering time.

Incongruent dissolution of clays and sediments results in the formation of zeolite and feldspathoid solids that incorporate Cs and Sr. Morphology and chemical composition of the secondary solids are examined using SEM, TEM, XRD, FTIR, NMR and XAS (e.g., Fig. 1). Of principal interest in the current study is the long-term stability of these secondary precipitates under conditions where the caustic waste source is removed.

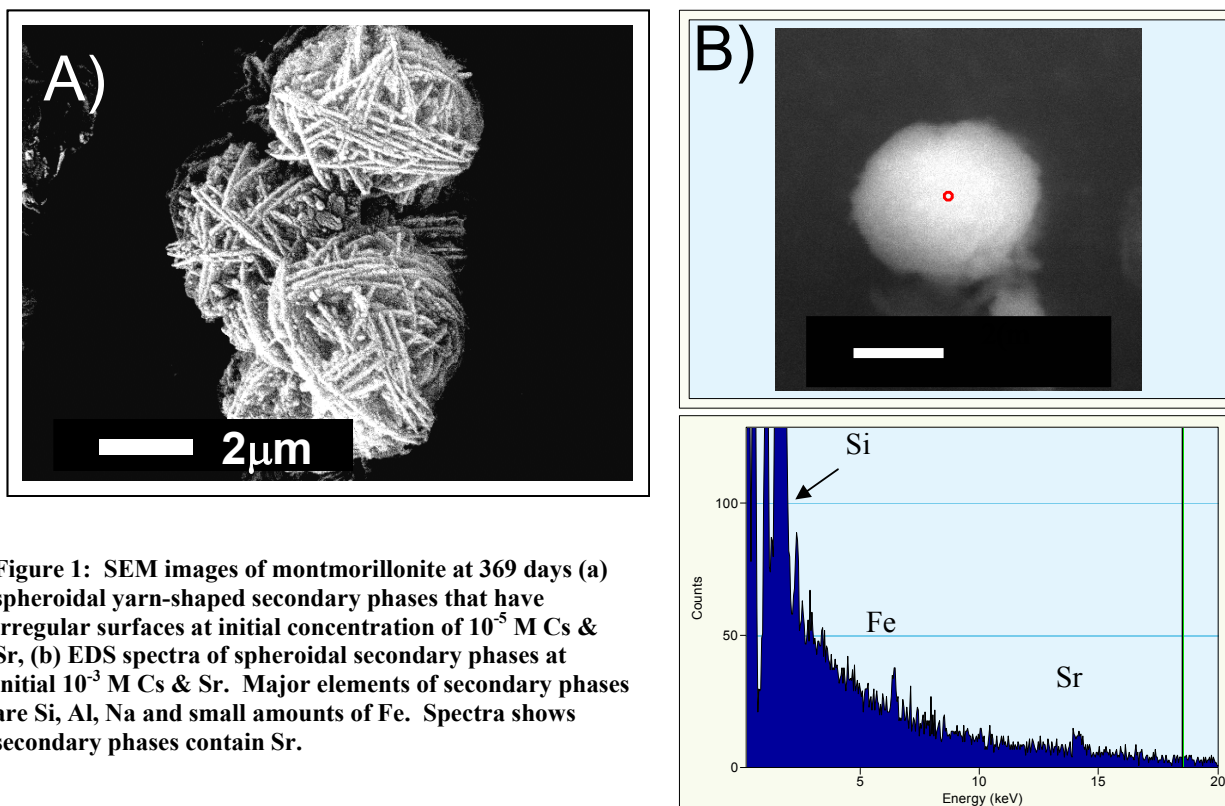


Figure 1: SEM images of montmorillonite at 369 days (a) spheroidal yarn-shaped secondary phases that have irregular surfaces at initial concentration of 10^{-5} M Cs & Sr, (b) EDS spectra of spheroidal secondary phases at initial 10^{-3} M Cs & Sr. Major elements of secondary phases are Si, Al, Na and small amounts of Fe. Spectra shows secondary phases contain Sr.

Dissolution Kinetics:

Specimen clays were reacted in batch systems with synthetic tank waste leachate (STWL) for 10 months prior to the initiation of desorption/dissolution experiments. The long-term release of radionuclide contaminants (in 0.01 M CaCl_2 solution at pH 8), from the precipitated solid phase was measured over the subsequent period. Results indicate that the precipitated solids are relatively recalcitrant; kinetics of Sr and Cs release are dependent upon the extent of mineral transformation during the sorption weathering phase in STWL (Fig. 2-3).

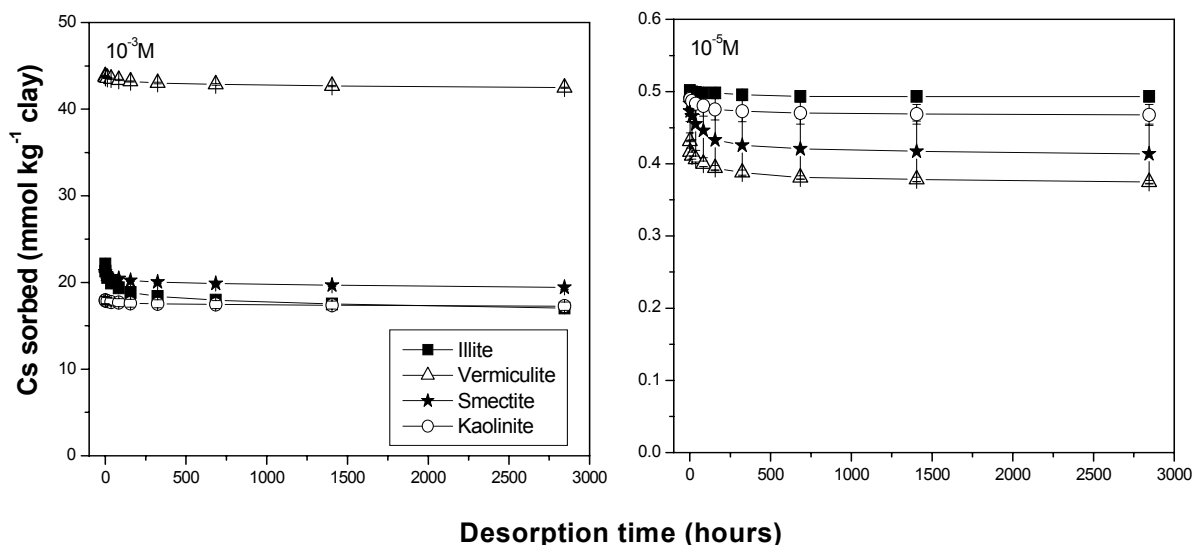


Figure 2: Dissolution of Cs from products of specimen clay weathering in STWL. Clays were reacted in STWL with Cs and Sr present as co-contaminants at concentrations of (a) 10^{-3} M and (b) 10^{-5} M.

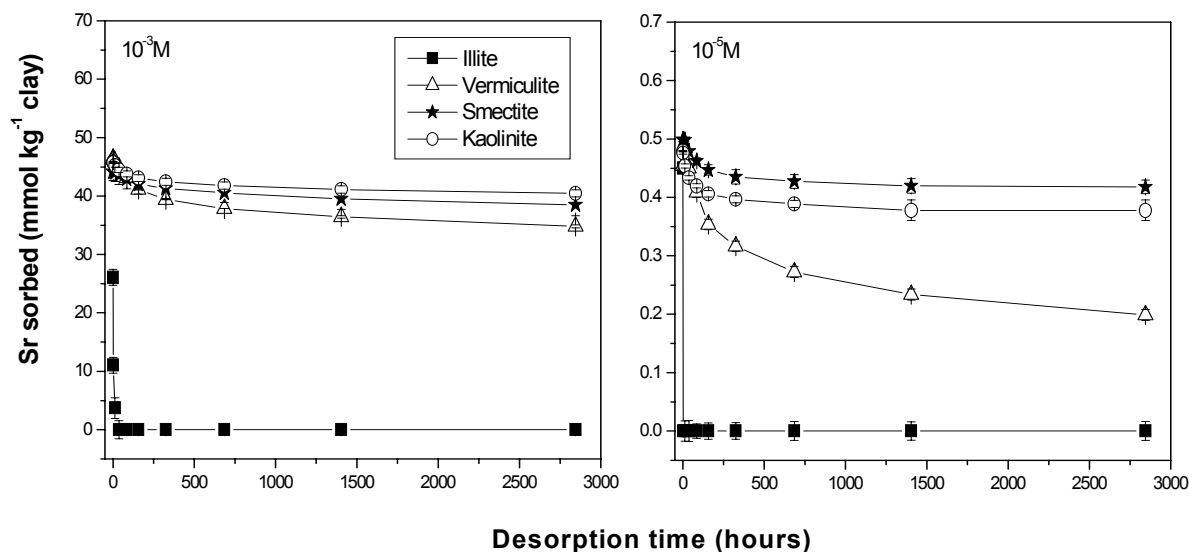


Figure 3: Dissolution of Sr from products of specimen clay weathering in STWL. Clays were reacted in STWL with Cs and Sr present as co-contaminants at concentrations of (a) 10^{-3} M and (b) 10^{-5} M.

Strontium release at circumneutral pH is correlated with the extent of mineral transformation occurring on during the weathering reaction. Data on mineral transformation rates are not shown here but see Chorover et al. (2003). Kaolinite and vermiculite, which show the greatest extent of incongruent dissolution over the 10 month period, retain the greatest fraction of Sr during the subsequent dissolution reaction (Fig. 3). Conversely, retention of Cs exceeds that of Sr for illite and vermiculite, presumably because of the high affinity sorption of Cs for charged siloxane in the interlayer of these clays.

NMR Spectroscopic Studies:

Progress has been made in the utilization of double- and triple-resonance solid-state NMR methods for the detection of specific-cation-containing phases in weathered clay samples. We have completed the first $^{29}\text{Si}/^{133}\text{Cs}$ double-resonance NMR studies in clay systems, utilizing a Cs-chabazite model system. The rotational-echo double-resonance (REDOR) NMR method proved superior to the Transfer of Populations in Double Resonance (TRAPDOR) NMR method in this system, answering an important question regarding the utility of each experiment, presumably due to the relatively small quadrupolar coupling constants for the cesium nuclei probed in this experiment. Figure 4 shows the NMR pulse sequences for REDOR and TRAPDOR, while the resulting REDOR spectra for Cs-CHA are displayed in Figure 5. In the REDOR experiment, the S_0 spectrum corresponds to the Fourier transform of a spin echo NMR signal acquired from the ^{29}Si nuclei in the sample without irradiation of the ^{133}Cs nuclei. The dephased, or S_f , signal arises from a similar spin-echo experiment but with rotor-synchronized spin perturbations (180 degree spin flips) of the ^{133}Cs species. The difference signal corresponds to ^{29}Si species with nearby ^{133}Cs nuclei, with the signal appearance predicated on the presence of through-space spin-spin dipolar couplings between the heteronuclei. To the best of our knowledge, this is the first reported $^{29}\text{Si}/^{133}\text{Cs}$ double-resonance NMR signal observed. We will now utilize this experiment in weathered clay systems to probe the location(s) of cesium ions within neophases formed under simulated tank waste leachate conditions.

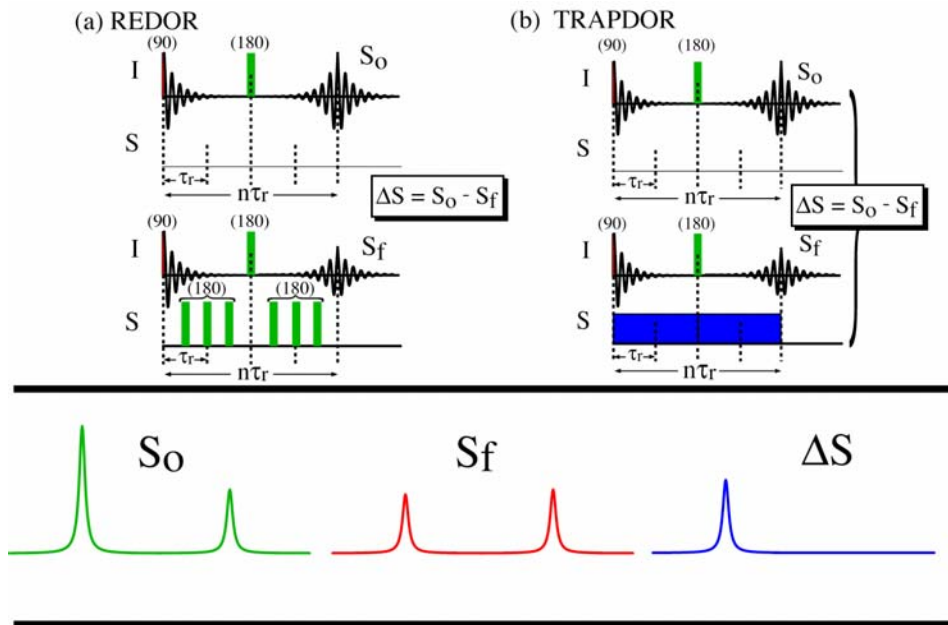


Figure 4: Radiofrequency pulse sequences used for (a) REDOR and (b) TRAPDOR NMR experiments

Solid-state NMR experiments will be run on samples acquired through homogeneous nucleation studies in collaboration with the Chorover group (see above). ^{23}Na , ^{27}Al , and ^{29}Si magic-angle spinning (MAS) data will be acquired using spectrometers at Penn State University. For the quadrupolar ^{23}Na and ^{27}Al nuclides, combinations of variable magnetic field strength (from 7.0 T to 11.7 T) and multiple quantum MAS (MQMAS) experiments will provide identification and quantification of phases present. The correlation of quadrupolar and chemical shift values to measured parameters from standard materials (zeolites, aluminas, and related solids) will aid in phase identification. Further, double- and triple-resonance MAS NMR experiments will provide local structural data from more complicated solid phases or amorphous regions.

We are also pursuing double- and triple-resonance experiments to detect the presence of strontium in original clay materials or neophases formed under weathering conditions. This necessitates the modification of existing solid-state NMR probes to reach the very low resonance frequency of ^{87}Sr (e.g., 21.671 MHz in an 11.7 T magnetic field). A new graduate

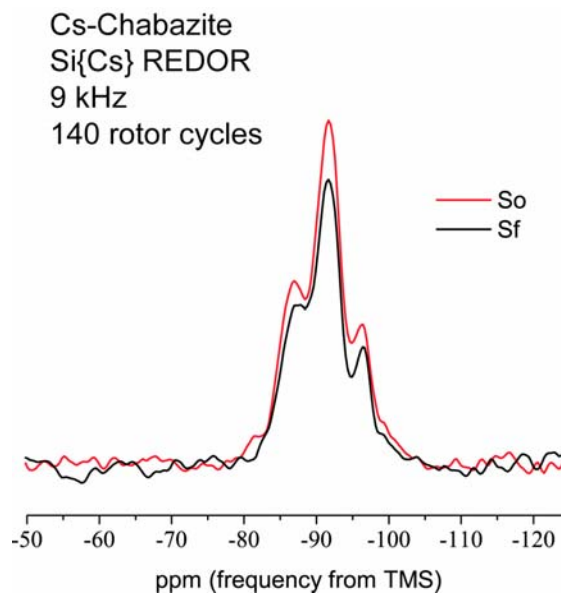


Figure 5: $^{29}\text{Si}/^{133}\text{Cs}$ echo and REDOR dephasing spectra from a sample of Cs-chabazite.

student is beginning on this project and is making electronic modifications to the probe systems. We have also obtained or synthesized model Sr containing compounds. Initial $^{29}\text{Si}/^{87}\text{Sr}$ and $^{27}\text{Al}/^{87}\text{Sr}$ double-resonance experiments will be accomplished during the next year of the project, followed by analyses of weathered clay systems containing cesium and strontium.

X-Ray Absorption Results: The extended X-ray absorption fine structure (EXAFS) spectra of kaolinite reacted with 10^{-3}M Sr and Cs for one day or 180 days show distinct differences in their local atomic structures (Fig. 6). Compared with reference Sr compounds, the spectrum of the kaolinite sample reacted for one day indicates that the mode of local Sr coordination is very similar to that of strontianite ($\text{SrCO}_3(\text{s})$). Least-squares best fits yield interatomic distances consistent with those of strontianite. Fitted Debye-waller factors (for fixed coordination number, N) are similar to those reported for freshly precipitated samples of strontianite (O'Day et al., 2000). In the sample aged for 180 days, there is no evidence for the presence of strontianite. Spectral features of this sample show some similarities to those of Sr in natural heulandite, but interatomic distances derived from least-squares fits for second-neighbor Al or Si atoms differ (Fig. 6). Trial-and-error fits to the 180-day spectrum indicate that the backscattering atoms are Al or Si and not a heavier atom; however, the low amplitude of these features suggests a poorly crystalline phase. The EXAFS interatomic distances are permissible with substitution of Sr into a number of different zeolite or aluminosilicate phases. Electron microscopy, XRD and geochemical modeling results suggest that prolonged aging time favors the formation of Sr silicate phases such as hydrated SrSiO_3 (Chorover et al., 2003).

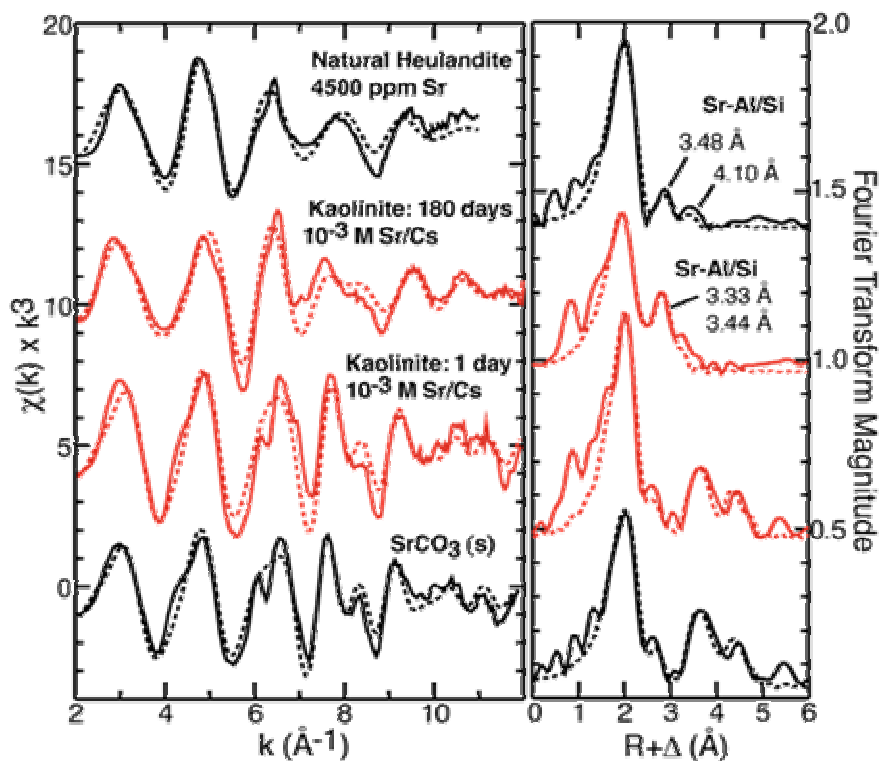


Figure 6: Sr K-edge EXAFS spectra of kaolinite weathered in STWL for 1 and 180 days, with reference to strontianite and heulandite.

Iodide Sorption and Transport Behavior in Hanford Sediments:

^{125}I radiotracer was used to study the sorption and transport behavior of iodide (I^-) species in batch and column systems containing Hanford sediments and a natural groundwater background solution. The calculated K_d values for iodide determined in duplicate batch adsorption tests are listed in Table 1. Sorption experiments indicated that iodide sorption was very low, consistent with the low sorption affinity of most soils/sediments for anions at neutral to high pH conditions.

The saturated column experiment was conducted with sediment C3177-110. The porewater velocity (v) and hydrodynamic dispersion coefficient (D) were 1.17 cm/day and 0.7 cm²/day, respectively. Because of the very low sorption of ^{125}I at this geochemical condition, ^{125}I transport behavior in the column was similar to that of the conservative tracer ^3H . However, small retardation of ^{125}I was noticeable in the first few pore volumes, and because the desorption of iodide (Um et al., 2003) exhibits a higher desorption K_d the trailing edge of the ^{125}I breakthrough curve lags the trailing edge of the ^3H at larger cumulative pore volumes. Iodide transport parameters were determined using CXTFIT code. The measured retardation factor of iodide in the column experiment was 1.08, leading to a calculated K_d value of 0.027 mL/g with 95 % confidence intervals (0.003 – 0.055). The K_d value determined from the column (pH=8.1) is an order of magnitude lower than those reported in Table 1, but similar to values determined in the previous batch sorption experiments with more alkaline pH conditions than the tests shown in Table 1. We have confirmed that the small adsorption tendencies of iodide in dilute natural waters onto Hanford sediments are sensitive and diminish as pH increases (Um et al., 2003).

Future column tests will use a highly alkaline simulated tank solution to ascertain whether caustic solution interactions with Hanford sediments leads to any secondary reactions that retard the migration of iodide aqueous species. That is, at very high pH conditions there may be sediment-tank liquor interactions that change the more common trends observed while using dilute solutions with slightly alkaline pH values. At this point there is little reason to repeat the column test using groundwater or alkaline low ionic strength solutions under unsaturated moisture conditions because there is no hint of any significant adsorption processes for such conditions.

Table 1. Sorption K_d s of ^{125}I with different sediments for an initial activity of 10 $\mu\text{Ci/L}$. (The K_d values are based on an average of two replicates.)

Radiotracer	Background	Sediments	Ave. K_d (mL/g)	pH
^{125}I	Groundwater	C3177-45	0.41	7.43
^{125}I	Groundwater	C3177-110	0.17	7.42
^{125}I	Groundwater	C3177-215	0.25	7.43

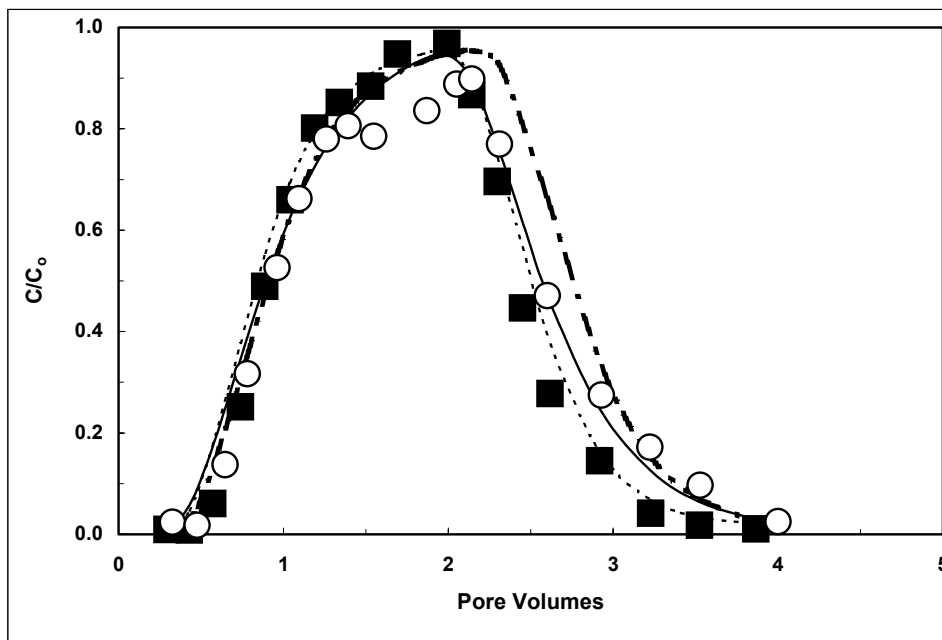


Figure 7. ^3H and ^{125}I Breakthrough Curves with Sediment C3177-110 and Hanford Groundwater. The relative concentrations of ^3H and ^{125}I in the effluent are represented by filled squares and open circles, respectively. The solid line represents the curve fit for the ^3H breakthrough data assuming equilibrium conditions. The dotted and the dashed-dotted lines represent the curve fits for the ^3H and ^{125}I breakthrough data, respectively, assuming nonequilibrium due to the presence of some immobile water domains or slow kinetics for adsorption-desorption.

Publications:

Um, W., R. J. Serne, and K. M. Krupka. Linearity and reversibility of iodide adsorption on sediments from Hanford, Washington under water saturated conditions, Submitted to Water Research (*in Review*), 2003.

Presentations:

Garry S. Crosson, Karl T. Mueller, Sunkyoung Choi, Mary K. Amistadi, and Jon Chorover, "Environmental Weathering of Aluminosilicate Clay Minerals: Solid-State NMR Studies of Transformations Leading to Radionuclide Sequestration", poster to be presented at *45th Rocky Mountain Conference on Analytical Chemistry*, Denver, Colorado, 26-30 July 2003.

Jon Chorover, Sunkyoung Choi, Garry Crosson and Karl Mueller, "Retention of Cs and Sr in solid-phase products of clay mineral weathering", invited talk for the 2003 Annual ACS meetings in New Orleans, March 2003.

References:

O'Day, P. A., Newville, M., Neuhoﬀ, P. S., Sahai, N., and Carroll, S. A (2000) X-ray absorption spectroscopy of strontium(II) coordination. I. Static and thermal disorder in crystalline, hydrated, and precipitated solids and in aqueous solution, *Journal of Colloid and Interface Science* **222**, 184-197.

Chorover, J., Choi, S., Amistadi, M. K., Karthikeyan, K. G., Crosson, G., and Mueller, K. T. (2003) Linking cesium and strontium uptake to kaolinite weathering in simulated tank waste leachate. *Environmental Science and Technology* **37**, 2200-2208.