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Project Title: **Interfacial Soil Chemistry of Radionuclides in the Unsaturated Zone**
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We are in the final year (in a one-year extension) of a project with the principal goal of investigating the impact of clay surface alteration, resulting from hydroxy-aluminum (HyA) and hydroxyaluminosilicate (HAS) species intercalation on reactivity of soils towards Cs and Sr. Special emphasis has been accorded to the unique geochemical conditions that are representative of the Hanford site vadose zone (high ionic strength, high pH, high Al concentrations). Specific objectives of the research include:
i) Quantify the rate and extent of contaminant sorption to prevalent soil minerals as a function of system composition and contaminant concentration.
ii) Determine the effects of intercalation of clays by HyA and HAS on the sorption/ion exchange process.
iii) Determine the role of NOM (dissolved and mineral bound) on the particle retention of Cs and Sr.
iv) Investigate the nature of mineral transformations induced by high pH and ionic strength conditions characteristic of waste impacted environments as it affects concurrent/subsequent retention of Cs and Sr.
v) Determine the coordination chemistry of contaminants bound into clay surfaces [as measured in objectives (i)-(iv)] using NMR and X-ray absorption spectroscopy (XAS)].

Significant progress has been made in achieving these objectives. We have conducted long-term kinetic studies - reaction times ranging from 1 to 370 d - to examine relationships between aluminosilicate weathering in the presence of synthetic tank waste leachate (STWL) and Cs/Sr uptake and release. Our experiments employ a sequence of specimen clay minerals including illite, vermiculite, smectite and kaolinite, which are also important reactive solids in the Hanford sediments (Serne et al., 2001). Parallel studies have been conducted with three representative Hanford sediment samples.

Sediments include coarse and fine sediments collected from the Hanford Formation (HC and HF, respectively) and Ringold Silt (RS). **These studies have shown direct coupling between mineral transformation reactions and contaminant sequestration/stabilization.**

Clays and sediments were reacted in batch systems with STWL in the presence of Cs^+ and Sr^{2+}, where both metals were present as co-contaminants at initial aqueous concentrations ranging from 10^{-5} to 10^{-3} M. The experiments presented here (for both sediments and clays) were conducted in aqueous suspension (50 g solid kg^{-1} suspension), in the presence of Na^+ (2.05 M), NO_3^- (1.0 M), $Al(OH)_4^-$ (0.05 M) and OH^- (1.0 M). At specified intervals, samples were removed for multifaceted analysis of "dissolved" (< 0.2 μm), "colloidal" (0.2-2 μm) and "solid phase" (> 0.2 μm) constituents. Solutions were analyzed for clay or sediment dissolution and uptake/release of Cs and Sr. Solids were analyzed for time-dependent changes in mineralogy. Here, we refer to neoformed solids that are produced in the reaction of sediments or clays with STWL as "secondary phases", though recognizing that the starting material for our experiments comprises secondary minerals (e.g., smectite, kaolinite) in the classical sense.

We had initially postulated that the formation of colloidal solids (from incongruent dissolution of native sediment minerals) might result in a significant colloidal fraction of lithogenic elements with possible incorporation of contaminant Cs and Sr. If mobile in STWL, this colloidal fraction could contribute significantly to radionuclide transport. We found that this was not the case for either specimen clay or sediment systems. For example, Fig. 1 shows the <2 μm colloidal plus dissolved (CD) fraction plotted against the <0.2 μm dissolved (D) fraction for several elements studied in the sediment experiments. All elements studied, with the exception of Fe, display virtually identical trends. Most notable is the 1:1 correspondence of CD and D values, as indicated by adherence to the 1:1 line and the strong linear correlation ($r^2 \geq 0.94$ within data sets). The close
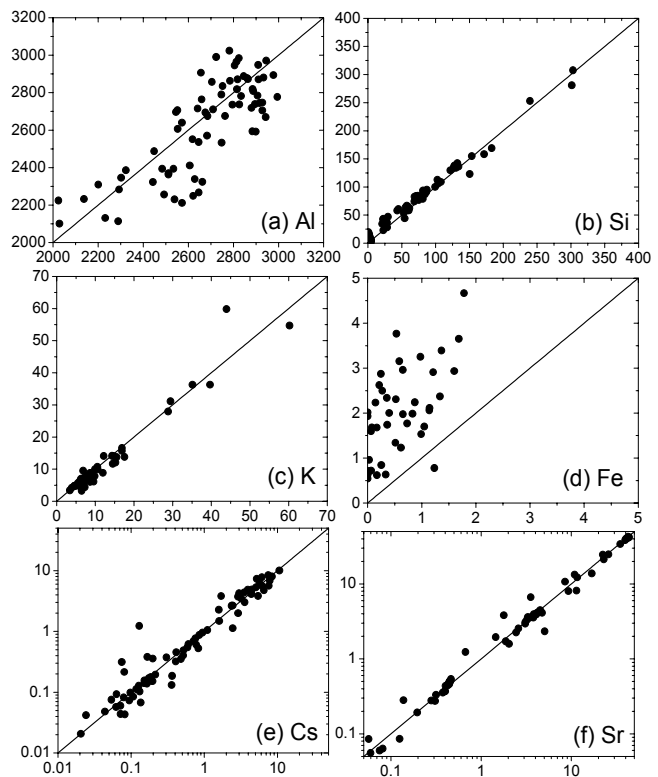

Figure 1. Colloidal plus dissolved (y axis) versus dissolved (x axis) concentrations (in mmol kg^{-1} of sediment) of lithogenic (Si, K, Fe) and contaminant (Al, Cs, Sr) elements following sediment-STWL reaction for 183 d. Close correspondence of the results indicates that aluminosilicate colloids are not stable in STWL, but rather flocculate and sediment as larger particles in the high ionic strength background. The exception is Fe, which shows significant enrichment in the colloidal fraction.

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agreement between concentrations in the CD and D pools indicates that, except for Fe, the colloidal pool is negligible and the dissolved pool is dominant. This is despite the fact that the formation of colloidal-sized precipitates was clearly observed using SEM. Evidently, these precipitates were either strongly bound to the surfaces of underlying sediment grains (i.e., surface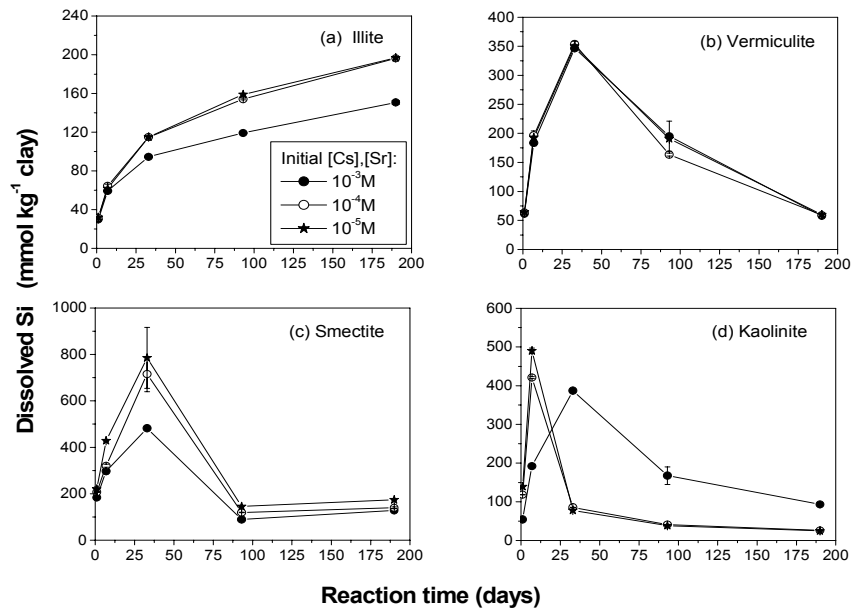 precipitates or heterocoagulates) or the colloids flocculated at the high ionic strength of STWL and these floccules sedimented along with the silt and sand sized particles. Although clearly not stable in STWL, it is plausible that the colloidal fraction may be mobilized by a reduction in aqueous ionic strength, upon removal of the STWL source. We plan to investigate that possibility in the next portion of the research. This is an important point because our data suggest that Cs and Sr are associated with these neoformed solids. Remaining discussion on aqueous phase reaction products is limited to the dissolved (< 0.2 μm) fraction.

Figure 2. Silicon dissolution during reaction of specimen clays with STWL (2.0 M Na^+, 1.0 M NO_3^-, 1.0 M OH^-, 0.05 M $Al(OH)_4^-$, pH 13.5, Cs & Sr = 10^{-5} to 10^{-3} M).

Dissolution of Si and its precipitation into secondary products plays a central role in the subsequent sequestration of radionuclides. The rate of Si release in clay and sediment systems was highly dependent on the mineralogy of initial solids. Initial dissolution of Si in the clay systems followed the order kaolinite > smectite > vermiculite > illite (Fig. 2).

Precipitation of Si occurs at clay-dependent threshold concentrations (Fig. 2), and results in time-dependent increases in short-range-ordered (SRO) secondary products, defined as such by their extraction in oxalate at pH 3 (Fig. 3). With aging time, these SRO phases are converted to more stable solids that exhibit increasing recalcitrance to extraction. This is most evident for the smectite and kaolinite systems, which show decreasing quantities of oxalate extractable Si with reaction time (Fig. 3).

Contaminant sorption to specimen clays and secondary reaction products is shown in Fig. 4 (Cs) and Fig. 5 (Sr). Strontium sorption exceeds that of Cs in all cases. Sorption of Cs to illite results rapidly in accumulation of a fraction that is non-exchangeable with Mg^{2+}, or with NH_4^+-oxalate during a 4 hr reaction time. The large residual fraction in illite is attributable to sorption to high-affinity frayed edge sites (FES). Sorption of Cs increases with time for the other three clay minerals. For vermiculite and smectite, the residual fraction is largely responsible for the increase, while in kaolinite, both residual and oxalate extractable pools contribute to long-term sorption trends (Fig. 4).
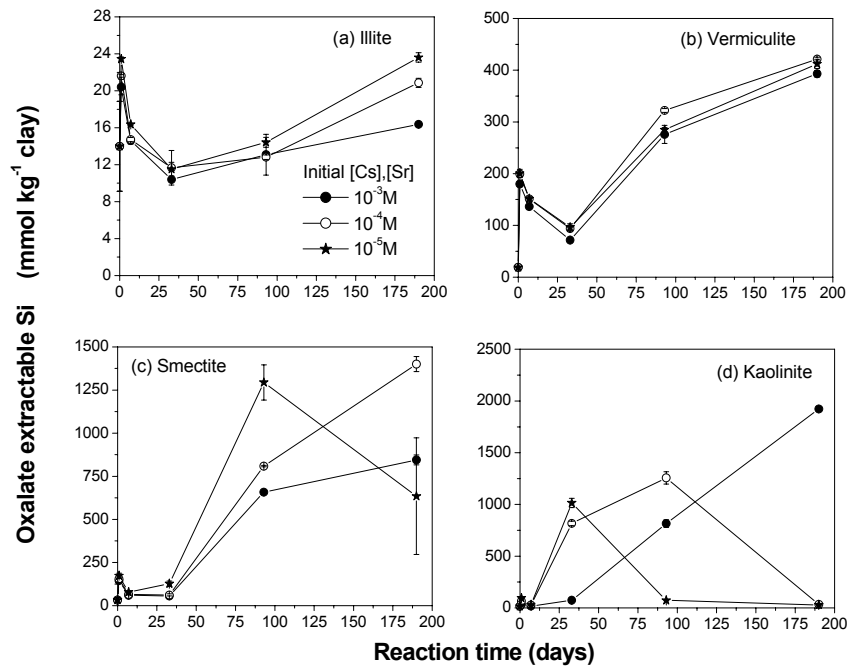

Figure 3. Time series trends in oxalate extractable ("short-range-ordered") silicon for the four specimen clays and three initial Cs and Sr concentrations. STWL (2.0 M Na^+, 1.0 M NO_3^-, 1.0 M OH^-, 0.05 M $Al(OH)_4^-$, pH 13.5, Cs & Sr = 10^{-5} to 10^{-3} M).

Nearly 100% sorption of Sr occurs irrespective of clay type and reaction time (Fig. 5). However, Sr behavior shows a stronger dependency on mineral dissolution and precipitation reactions, as reflected in the close correspondence between oxalate extractable amounts of Si (Fig. 2) and Sr (Fig. 5). For both smectite and kaolinite systems, a trajectory of sorbed Sr from dominantly exchangeable to short-range-ordered, and finally to residual forms parallels the trends for the dissolution and reprecipitation of Si with Al from the STWL (Si precipitation results in a decrease in dissolved Al also). For example, the dramatic increase in residual (non-extractable) Sr in kaolinite systems at 190 d and 10^{-4} M initial Sr (Fig. 5d) coincides with a large drop in SRO silicon phases (open symbols in Fig. 3d). Although we recognize the shortcomings associated with uncritical use of chemical extraction methods, our approach is to combine the quantitative power of wet chemical methods with electron microscopy and molecular spectroscopy studies (NMR, FTIR, XAS) *on the same samples* to help us to discern the precise nature of material extracted. **The integrated use of macroscopic, microscopic and spectroscopic techniques will continue to be a key component of our research approach.**
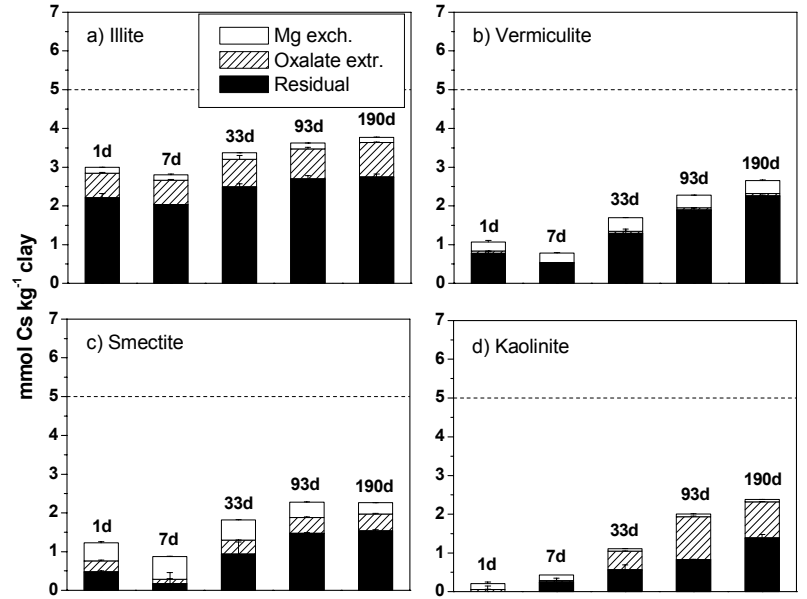

Figure 4. Time-dependent sorption of Cs into (i) exchangeable, (ii) oxalate extractable and (iii) residual pools during reaction with the four specimen clays (10^{-4} M Cs initial concentration). Dotted line represents 100% sorption.
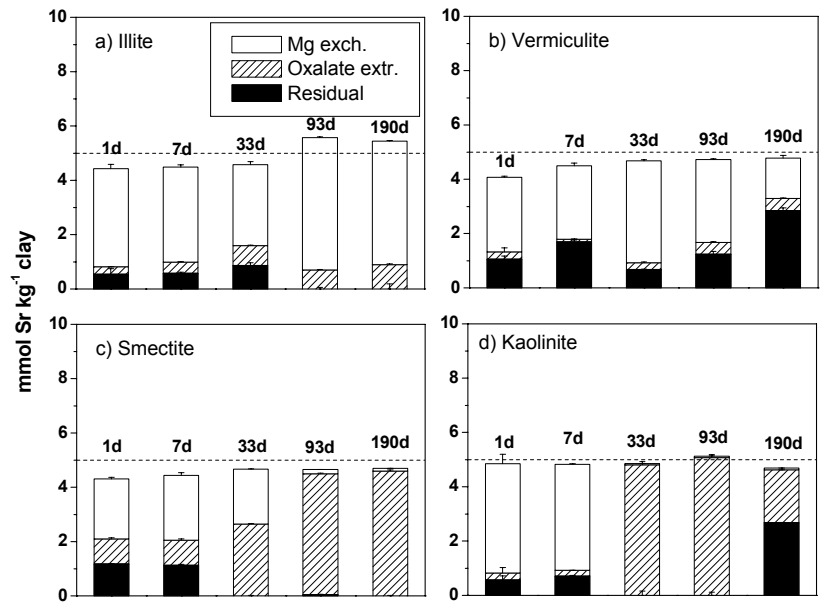

Figure 5. Time-dependent sorption of Sr into (i) exchangeable, (ii) oxalate extractable and (iii) residual pools during reaction with the four specimen clays (10^{-4} M Sr initial concentration). Dotted line represents 100% sorption.

Despite the high background Na^+ concentration in the systems (2000 to 200,000 times that of the radionuclides), mineral dissolution and precipitation reactions were found to be depend strongly on Cs^+ and Sr^{2+} concentrations (Fig. 2-3). Except for vermiculite, whose weathering showed only small dependence on Cs and Sr concentration, the kinetics of Si dissolution and the rate of subsequent precipitation of secondary SRO solids both decreased with increasing Cs and Sr concentration. As suggested by Fig. 3, this contaminant effect also influences the time required for transformation of SRO
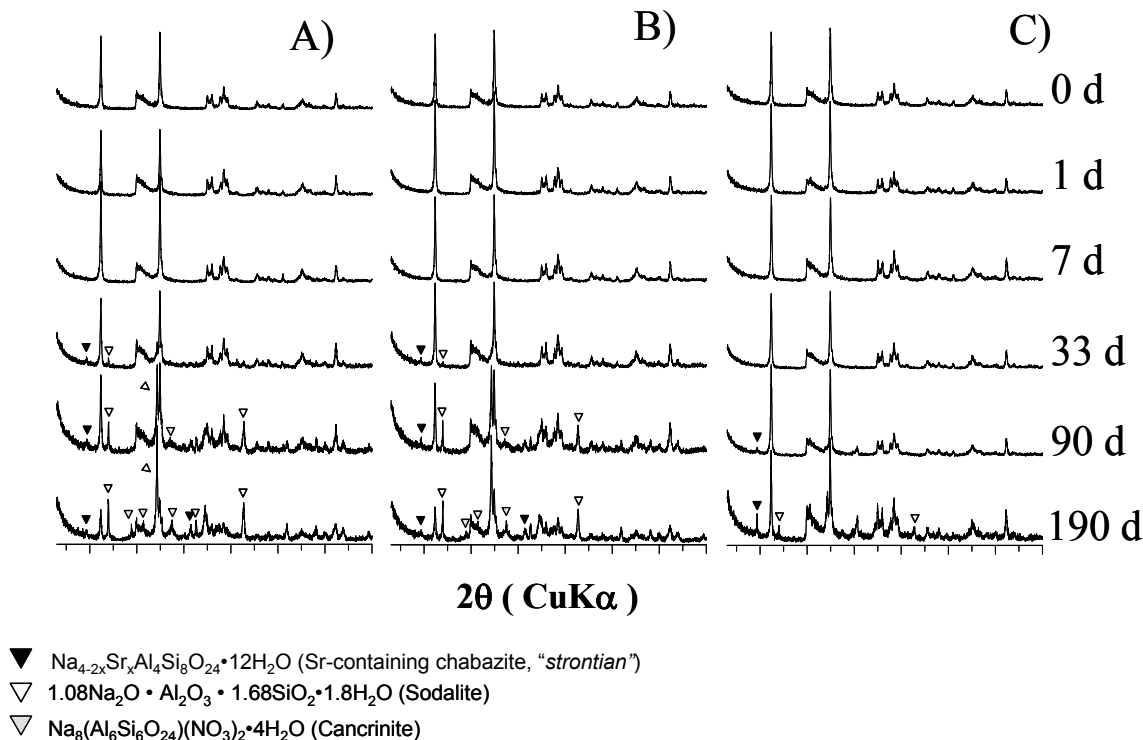

▼ $Na_{4-2x}Sr_xAl_4Si_8O_{24}$•$12H_2O$ (Sr-containing chabazite, "*strontian*")
▽ $1.08Na_2O$ • Al_2O_3 • $1.68SiO_2$•$1.8H_2O$ (Sodalite)
▽ $Na_8(Al_6Si_6O_{24})(NO_3)_2$•$4H_2O$ (Cancrinite)

Figure 6. X-ray diffraction patterns of randomly-oriented, unreacted kaolinite and reacted kaolinite (1-190 days) at Cs and Sr concentrations of (a) 10-5 M (b) 10-4 M (c) 10-3 M. XRD peaks for newly developed secondary precipitates are marked as Sr-chabazite, sodalite , and cancrinite.

phases into more stable, non-extractable and crystalline products. For example, Fig. 6 (kaolinite) shows that (i) the types of x-ray detectable (crystalline) secondary phases and (ii) the rate of their formation are dependent on contaminant concentration: (i) chabazite forms first, followed by sodalite and finally cancrinite, with the latter forming only at the lower Cs and Sr concentrations, and (ii) the solids are detected earliest at lower contaminant concentration.

Diffuse reflectance Fourier transform infrared spectra (DRIFT) of the same reacted kaolinite samples - after thorough washing with ethanol to remove entrained solution - (Fig. 7) show the presence of nitrate as an anionic constituent in the secondary solid phases. New bands at 1384 and 1422 cm^{-1} were observed in kaolinite, smectite and all reacted sediments after 1 month (clays) or longer (sediments) reaction time. These bands began to emerge after 92 d for Hanford coarse and Ringold sediments, while the bands were only visible in Hanford fine sediments after 374 d. The two sharp peaks were accompanied by a broad shoulder or band at 1480 cm^{-1} in all sediments at 10^{-5} M Cs and

Sr. Broad but more intense bands developed at slightly higher frequencies of 1498-1510 cm^{-1} at 10^{-4} and 10^{-3} M Cs and Sr loadings. These bands are characteristic of nitrate stretching. The band at 1384 is identical to that for KNO$_3$. A weak band at 730 cm^{-1} clearly emerged over time for Hanford coarse and Ringold sediments, which is in the region of nitrate (N-O) in-plane bending and bands at 878 or 858 cm^{-1} (N-O out of plane bending) appeared in all sediments, kaolinite and smectite, mainly at the higher Cs and Sr loadings after 374 d. In conjunction with the XRD data,
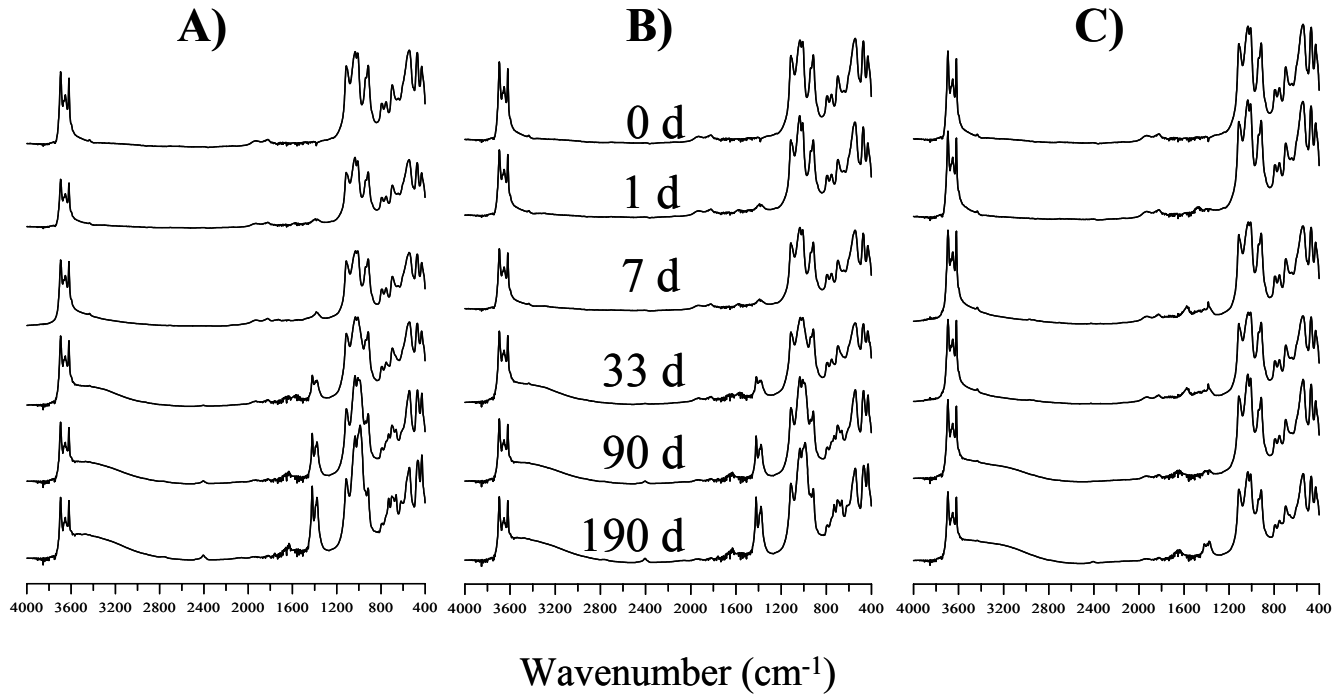

Figure 7. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of unreacted and time-series of reacted kaolinite samples at three contaminant concentrations: (a) Cs and Sr = 10^{-5} M, (b) Cs and Sr = 10^{-4} M, (c) Cs and Sr = 10^{-3} M.

the DRIFT results indicate the formation of nitrate-bearing zeolite-feldspathoids (nitrate-cancrinite) in both specimen clay and sediment systems. Phyllosilicate transformation to zeolites is further supported by integrated peak intensities in ^{27}Al magic angle spinning (MAS) NMR spectra for the kaolinite systems that clearly differentiate between six-fold coordinated Al (Al^{VI}, kaolinite) and four-fold coordinated Al (Al^{IV}, zeolite) as a function of reaction time and contaminant concentration (Fig. 8).

This finding may prove crucial to stabilization of radionuclide contaminants in the waste-impacted vadose zone for two reasons. First, the presence of high NO$_3^-$ concentrations in tank waste leachate appears to be promoting the formation of stable ^{137}Cs and ^{90}Sr sequestering solid phases (Cs and Sr can be bound into exchange sites
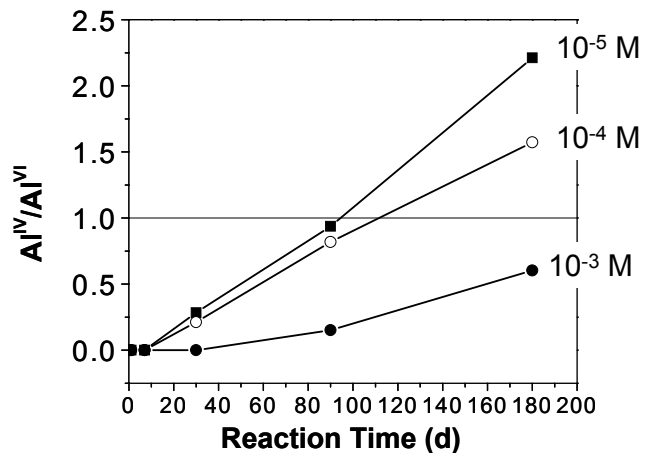

Figure 8. Al(IV)/Al(VI) ratio in reacted kaolinite over time measured by NMR. The ratio increases over time, indicating the relative increase of four-fold coordinated Al.

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on neoformed zeolites, as discussed more below).   Second, the thermodynamically

favorable species of another high risk radionuclide, iodine-129, under tank waste conditions is $^{129}IO_3^-$ and this ion may substitute for NO_3^- during formation of secondary solids. Both of these issues will be explored further in future research.

DRIFT spectra of reacted clays and sediments also showed a shift in peak location of the Si-O-Si vibration band to lower wavenumber (e.g., for sediments from ca. 1028 to 1001 cm^{-1} with increasing reaction time. This shift reflects an increased preponderance of Si-O-Al bonds during formation of secondary solids in the presence of Al-rich STWL. Scanning electron microscopy (SEM, Fig. 9) and energy dispersive x-ray spectroscopy (EDS) provided direct evidence of zeolite formation and suggests Sr incorporation into neoformed solids (Fig. 10).

Figure 9. Scanning electron micrographs of progressive secondary solid phase formation in smectite (montmorillonite) systems: (a) 7 d reaction at 10^{-3} M Cs and Sr, (b) (a) 30 d reaction at 10^{-3} M Cs and Sr, (c) 90 d reaction at 10^{-4} M Cs and Sr, and (d) 190 d reaction at 10^{-5} M Cs and Sr.

The time dependent changes in Sr coordination that accompany transformation from exchangeable to non-extractable forms are clearly reflected in extended x-ray absorption fine structure (EXAFS) spectra (Fig. 11). The results show that Sr is initially present in an adsorption complex comparable in structure to $SrCO_3$, but at reaction times between 1 and 6 months, Al or Si atoms are observed in the second shell, reflecting Sr incorporation into zeolite. The EXAFS spectrum for 180 d is similar to that for Sr zeolites.

As a result of high energy of the Cs K edge and elemental interferences at the L edge, we have not been able to obtain
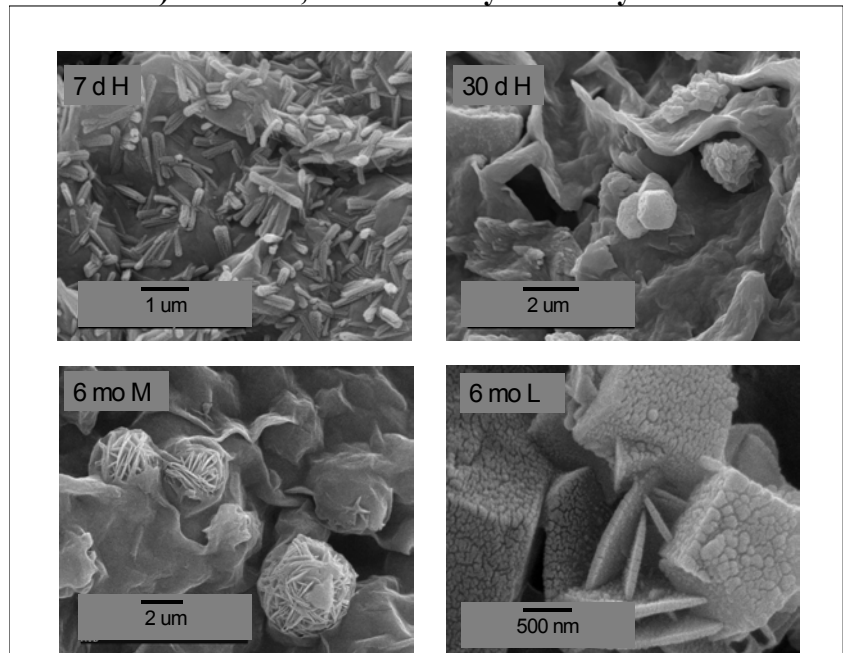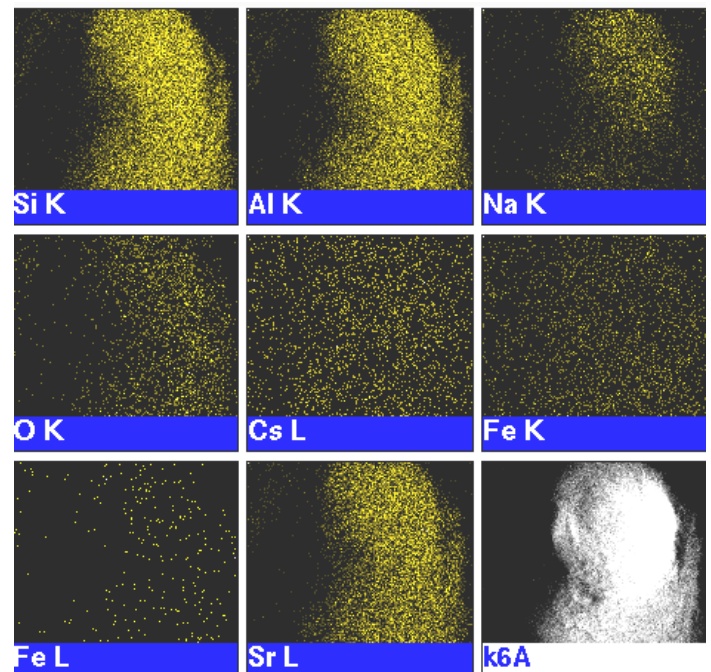

Figure 10. EDS mapping of a chabazite crystal formed after 6 months in kaolinite systems shows clear incorporation of Sr into the aluminosilicate structure, whereas Cs is more diffusely distributed throughout the matrix.
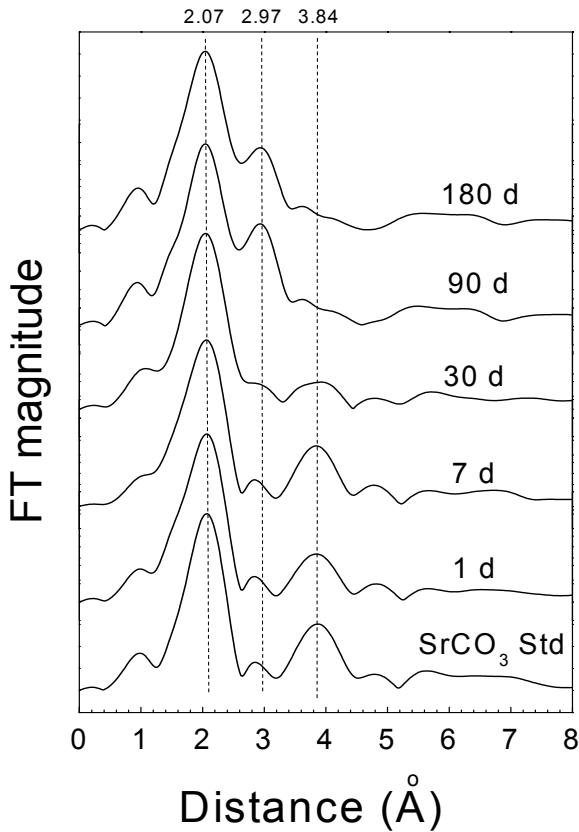
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Figure 11. Time series of Sr K edge EXAFS spectra (uncorrected for phase shift) of kaolinite reacted with 10^{-3} M Cs/Sr. Data show a time-dependent change in second nearest neighbor peak.

reliable EXAFS spectra for the low Cs concentrations in reacted samples. However, we have used EXAFS to show preferential retention of Cs in inner-sphere complexes on Cs saturated smectite and vermiculite clays that are subjected to progressive exchange with Na^+ (Bostick et al., 2002). In addition, we have made significant progress in elucidating Cs binding interactions with 2D heteronuclear correlation methods of nuclear magnetic resonance (NMR) spectroscopy, such as transfer or populations double resonance (TRAPDOR). A $^{29}Si/^{133}Cs$ TRAPDOR spectrum for reacted kaolinite shows two ^{29}Si resonances with the -92 ppm peak corresponding to kaolinite and the -87 ppm peak corresponding to the zeolite phases formed in during reaction (Black line in Fig. 12). Application of a dephasing pulse for ^{133}Cs results in a decrease in the ^{29}Si resonance for kaolinite but no change in that for the zeolite, suggesting that in these systems, Cs is more strongly associated with kaolinite than with the newly formed solids, a result that is in agreement with other data (e.g., Fig. 10).

Heteronuclear Correlation NMR Studies: $^{29}Si/^{133}Cs$ TRAPDOR Experiments

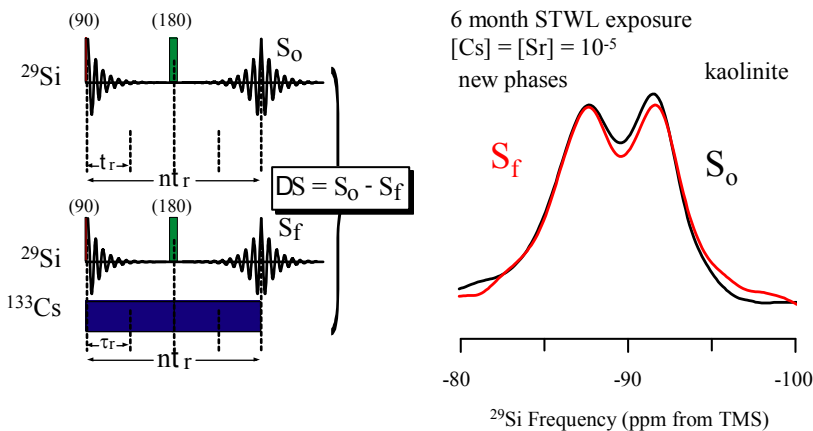Results of our work to date strongly suggest that Sr is strongly incorporated into neoformed secondary solids during reaction of both specimen clays and Hanford sediments with tank waste leachate, whereas Cs uptake is more strongly impacted by the presence of high affinity sites in the clays themselves. Although Cs does not clearly bind into the new solids, patterns of increasing sorption over long time scales (Fig. 4)

Figure 12. $^{29}Si/^{133}Cs$ TRAPDOR spectra of kaolinite reacted with STWL in the presence of 10^{-5} M Cs and Sr. Results indicate Cs is associated with kaolinite to a greater extent than with newly formed phases, but potential Cs mobility (which may mask sorption) in zeolites is being probed in variable temperature experiments.

are consistent with diffusion-limited transport to high energy sites which may be occluded during long-term weathering of sediments and clays.

Presentations, Publications and Theses

Presentations

Chorover, J., S. Choi, K. Mueller, G. Cresson, and K. G. Karthikeyan. 2001. Sequestration of Cs and Sr during weathering of aluminosilicate clays at high pH. ACS National Meeting, Chicago, IL, August, 2001.

Rotenberg, P., S. Choi, M. K. Amistadi and J. Chorover. 2001. Reaction of radionuclides in Hanford Sediments under simulated tank waste leachate conditions. ACS National Meeting, Chicago, IL, August, 2001.

Serne, R.J., C.W. Lindenmeier, and H. T. Schaef. 2001. Geochemical Conditions in the Vadose Zone Under Leaking Tanks at B-BX-BY Area. ACS National Meeting, Chicago, IL, August, 2001.

Mueller, K., G. Crosson, S. Choi, M. K. Amistadi, and J. Chorover. 2001. Solid-state NMR studies of clays subjected to a simulated tank waste leachate. Soil Sci. Soc. Am. Annual Meetings, Charlotte, NC, October, 2001.

Choi, S., J. Chorover, K. Muller, K.G. Karthikeyan, G. Grosson and M.K. Amistadi. 2001. Weathering behavior and Cs/Sr uptake of clays under extreme geochemical conditions, The 38th Clay Mineral Society National Meeting, 16-20 June, Wisconsin MD.

Chorover, J., K. G. Karthikeyan, and S. Choi. 2000. Reaction of cesium and strontium in aqueous colloidal aluminosilicate systems at high pH. Annual meetings of the American Geophysical Union, San Francisco, CA., December 2000.

Ainsworth, C. C., R. J. Serne, J. P. McKinley, H.T. Schaef, and J. M. Zachara. 2000. Hanford Sediments Under the SX-108 High-Level Waste Tank: Current Geochemical Status. Annual meetings of the American Geophysical Union, San Francisco, CA., December 2000.

Serne, R. J., C. W. Lindenmeier , and H. T. Schaef . 2000. Geochemical Conditions in the Vadose Zone at Leaking Single-Shell Tanks in the B-BX-BY Waste Management Area in Hanford's 200 E Area. Annual meetings of the American Geophysical Union, San Francisco, CA., December 2000.

Chorover, J., K. G. Karthikeyan, K. T. Mueller, T. Lalain, and A. Vairavamurthy. 2000. Interfacial chemistry of cesium and strontium in alkaline, aqueous systems. International Workshop on Surface Chemical Processes in Natural Environments, Monte Verita, Switzerland, October 2000.

Rotenberg, P., S. Choi, K. G. Karthikeyan, and J. Chorover. 2000. Uptake of Cs and Sr by Hanford sediments at high pH and ionic strength. Soil Science Society of America Annual Meetings. Minneapolis, MN. November, 2000.

Theses

Rotenberg, P. A. 2002. Reaction of cesium and strontium in Hanford Sediments under tank waste leachate conditions. M.S. Thesis in Soil Science, The Pennsylvania State University, May 2002.

Crosson, G. 2003 (expected). Solid-state NMR studies of weathered clays: Implications for environmental contamination. Ph.D. Thesis in Chemistry, The Pennsylvania State University.

Publications and Reports Completed

Bostick, B. C., M. A. Vairavamurthy, K. G. Karthikeyan and J Chorover. 2002. Cesium adsorption on clay minerals: An EXAFS spectroscopic investigation. *Environ. Sci. Technol.* (*In review post revision*).

Chorover, J., S. Choi, G. Crosson, K. G. Karthikeyan, M. K. Amistadi, and K. T. Mueller. 2002. Mineral transformation in colloidal kaolinite suspensions under tank waste leachate conditions. *Environ. Sci. Technol.* (In revision).

Serne RJ, HT Schaef, BN Bjornstad, BA Williams, DC Lanigan, DG Horton, RE Clayton, VL LeGore, MJ O'Hara, CF Brown, KE Parker, IV Kutnyakov, JN Serne, AV Mitroshkov, GV Last, SC Smith, CW Lindenmeier, JM Zachara, and DB Burke. 2002. *Characterization of Uncontaminated Vadose Zone Sediment from the Hanford Reservation - RCRA Borehole Core Samples and Composite Samples*. PNNL-13757-1, Pacific Northwest National Laboratory, Richland, Washington

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Serne RJ, GV Last, GW Gee, HT Schaef, DC Lanigan, CW Lindenmeier, RE Clayton, VL LeGore, RD Orr, MJ O'Hara, CF Brown, DS Burke, AT Owen, IV Kutnyakov, and TC Wilson. 2002. G*eologic and geochemical data collected from vadose zone sediments from Borehole SX 41-09-39 in the S/SX Waste Management Area and preliminary interpretations*. PNNL-13757-3, Pacific Northwest National Laboratory, Richland, Washington.

Serne RJ, GV Last, HT Schaef, DC Lanigan, CW Lindenmeier, CC Ainsworth, RE Clayton, VL LeGore, MJ O'Hara, CF Brown, RD Orr, IV Kutnyakov, TC Wilson, KB Wagnon, BA Williams, and DB Burke. 2002. G*eologic and geochemical data and preliminary interpretations of vadose zone sediment from Slant Borehole SX-108 in the S-SX Waste Management Area*. PNNL-13757-4, Pacific Northwest National Laboratory, Richland, Washington.

Publications in Preparation

Choi, S. and J. Chorover. xxxx. Weathering of illite, vermiculite and montmorillonite under tank waste leachate conditions For submission to *Appl. Geochem.* (in advanced prep.).

Rotenberg, P. A., R. J. Serne and J. Chorover. xxxx. Reaction of cesium and strontium in Hanford sediments at high pH in synthetic tank waste leachate.

Rotenberg, P. A., R. J. Serne and J. Chorover. xxxx. Effects of contaminant aging on cesium and strontium desorption following reaction of Hanford sediments with caustic waste solutions.

Crosson, G. S., M. K. Amistadi, J. Chorover, and K. T. Mueller. xxxx. Solid-state NMR studies of the weathering of kaolinite under simulated tank waste conditions. For submission to *J. Phys. Chem*.