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*Project Title: **Interfacial Soil Chemistry of Radionuclides in the Unsaturated Zone***

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This is 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 d to 2 yr - 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 in both specimen clay and Hanford sediment systems.**

In the previous annual report, we emphasized geochemical behavior of the specimen clay systems. In this report, we summarize some of the quantitative results regarding mineral dissolution and sorption behavior in the whole sediment systems.

Weathering and Contaminant Sorption in Hanford Sediments:

Uncontaminated sediments from Hanford, WA (Hanford coarse, HC; Hanford fine, HF; Ringold silt, RS) were reacted with a synthetic tank waste leachate (composition 0.05 M NaAlO₂, 2 M Na⁺, 1 M NO₃⁻, 1 M OH⁻ (pH ~13.7), Cs and Sr concentrations 10⁻⁵ to 10⁻³ M) that approximates the aqueous chemistry of tank leachate at Hanford, WA. Batch experiments were conducted to measure long term kinetics of Cs and Sr uptake, from 1 to 374 days of exposure to the synthetic tank waste leachate. Dissolution and precipitation of Al and Si were also measured to assess the potential role of mineral dissolution and coprecipitation in radionuclide uptake. Mineral transformations were monitored using a combination of selective extraction, XRD, SEM, FTIR and TGA methods. Sediments began to dissolve rapidly at the high experimental pH, releasing Si to solution. A sharp decrease in soluble Si after 29 d corresponded to the precipitation of poorly crystalline aluminosilicate solids (Fig. 1). Silicon dissolution and re-precipitation with Al (Fig. 2) were greatest in Ringold sediments, which contain the highest amount of clay.

SEM images showed weathered surfaces and the formation of crystalline secondary solid phases in all sediments after 183 d. Based on morphologies observed in studies conducted under similar conditions, these formations were likely nitrate-cancrinite. DRIFT spectra confirmed the presence of nitrate-bearing minerals by band formation in the nitrate-stretching region after 374 d. XRD did not provide clear evidence of new crystalline solid phases at any reaction time; evidently neoformed solids were below detection and/or insufficiently crystalline for detection by XRD. Significant Cs and Sr sorption occurred, despite high ionic strength. Cs sorption fluctuated over time (Fig. 3), whereas Sr uptake clearly increased (Fig. 5). Sorbent affinity for Cs and Sr at short time intervals occurred in the order RS > HF > HC (Fig. 4). However, all sediments had similar Sr uptake capacities after reactions progressed for several months (Fig. 5). By 374 d, Sr uptake in all sediments exceeded that of Cs, with 80-93% and 15-37% uptake, respectively. Strontium became progressively recalcitrant to desorption after 92 d, suggesting significant Sr coprecipitation in sediment-STWL environments. Cs retention by sediments did not follow obvious time dependent trends.

We are in the process of writing manuscripts based on the whole sediments studies. The range of behaviors observed in the specimen clay systems (e.g., see annual report for 2001-2002) provides an ideal reference for deducing coupled transformation and sorption reactions in the more complex sediments.

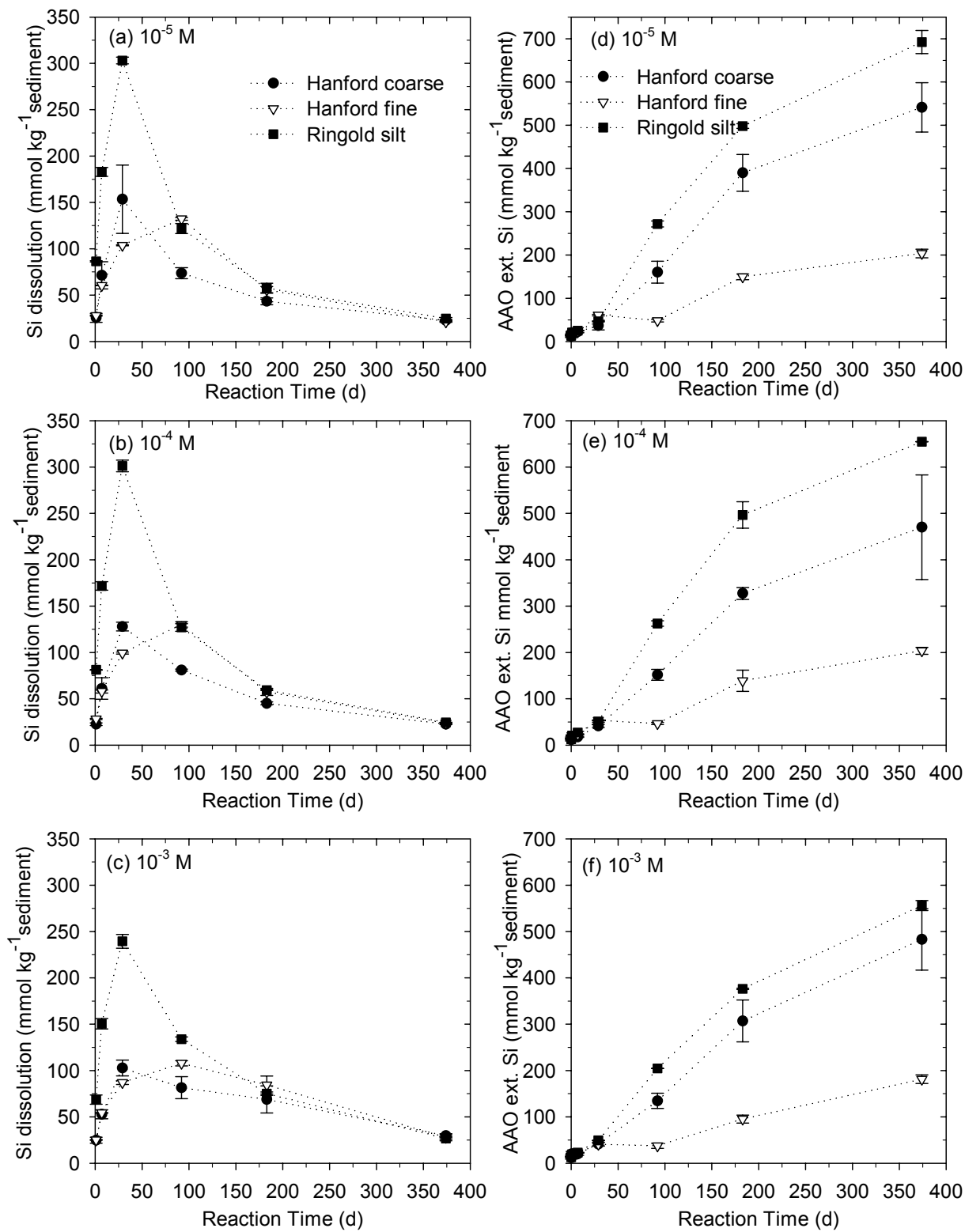


Figure 1. Time dependent dissolution and reprecipitation of Si in Hanford sediment systems reacted with synthetic tank waste leachate (STWL) solution.

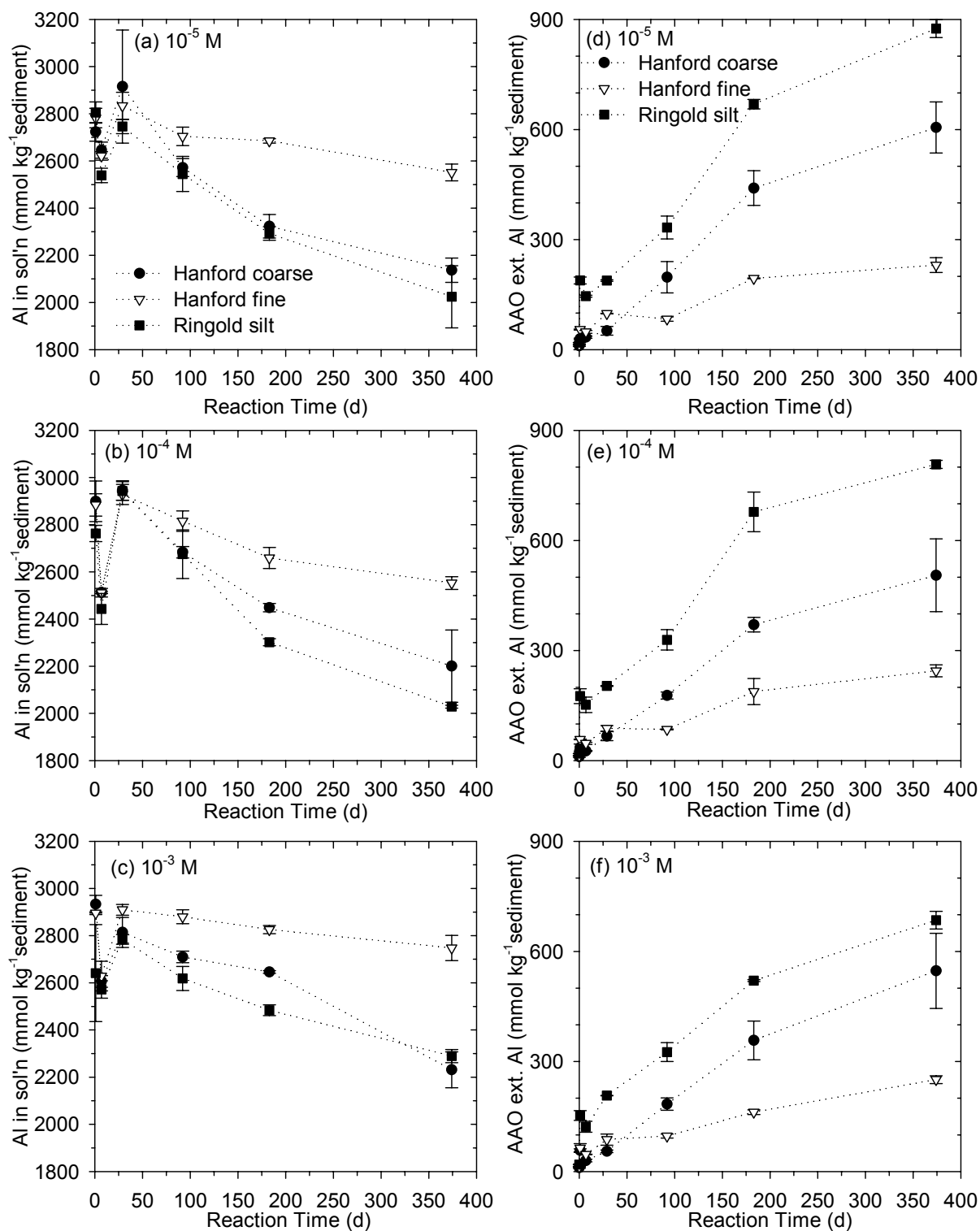


Figure 2. Time dependent dissolution and reprecipitation of Al in Hanford sediment systems reacted with synthetic tank waste leachate (STWL) solution.

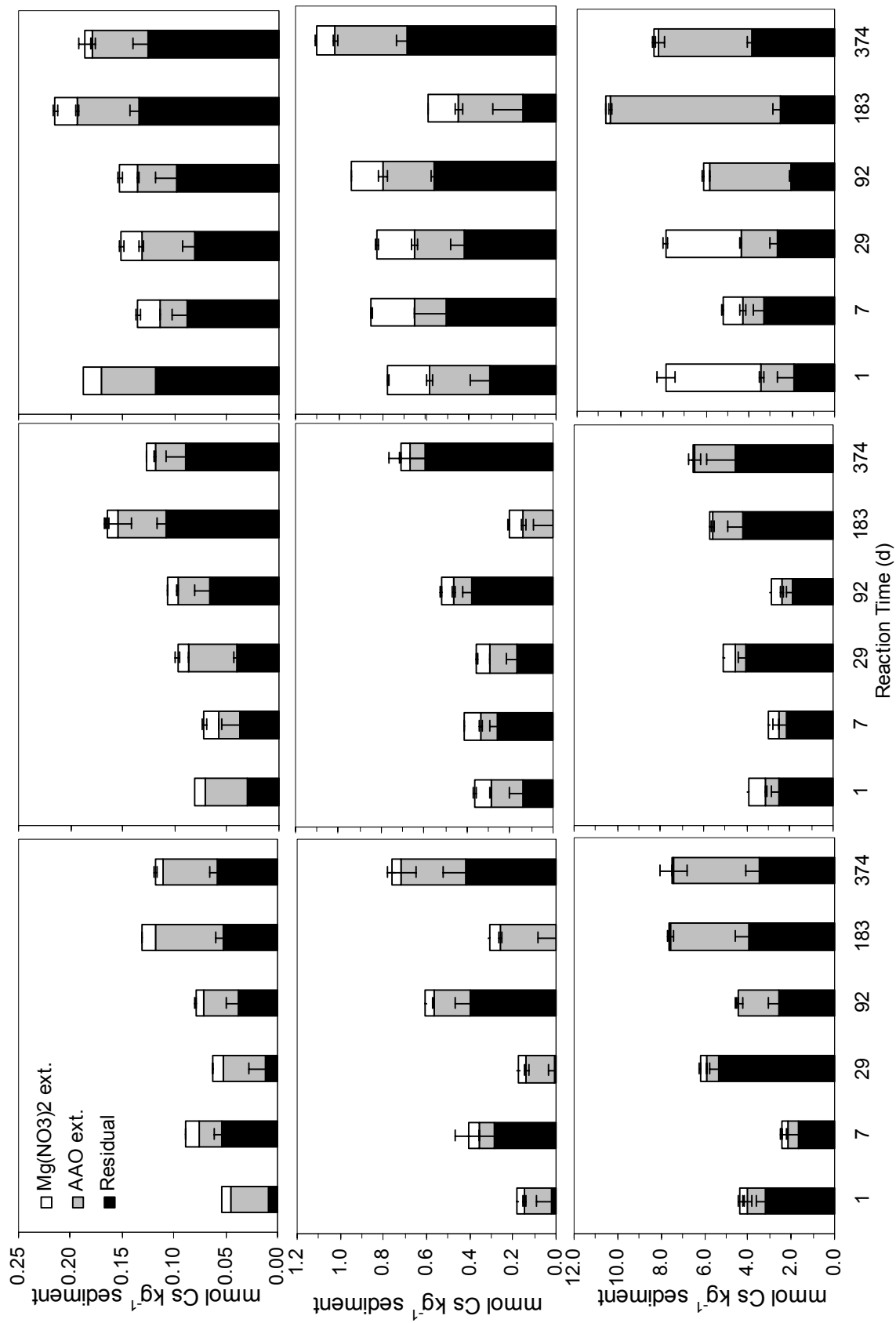


Figure 3. Sr partitioning determined by sequential extractions of HC, HF, RS sediments following reaction with STWL for 1 to 374 d. Initial Cs and Sr concentrations of (a) 10⁻⁵ M; (b) 10⁻⁴ M; (c) 10⁻³ M. Left to right: HC, HF, RS.

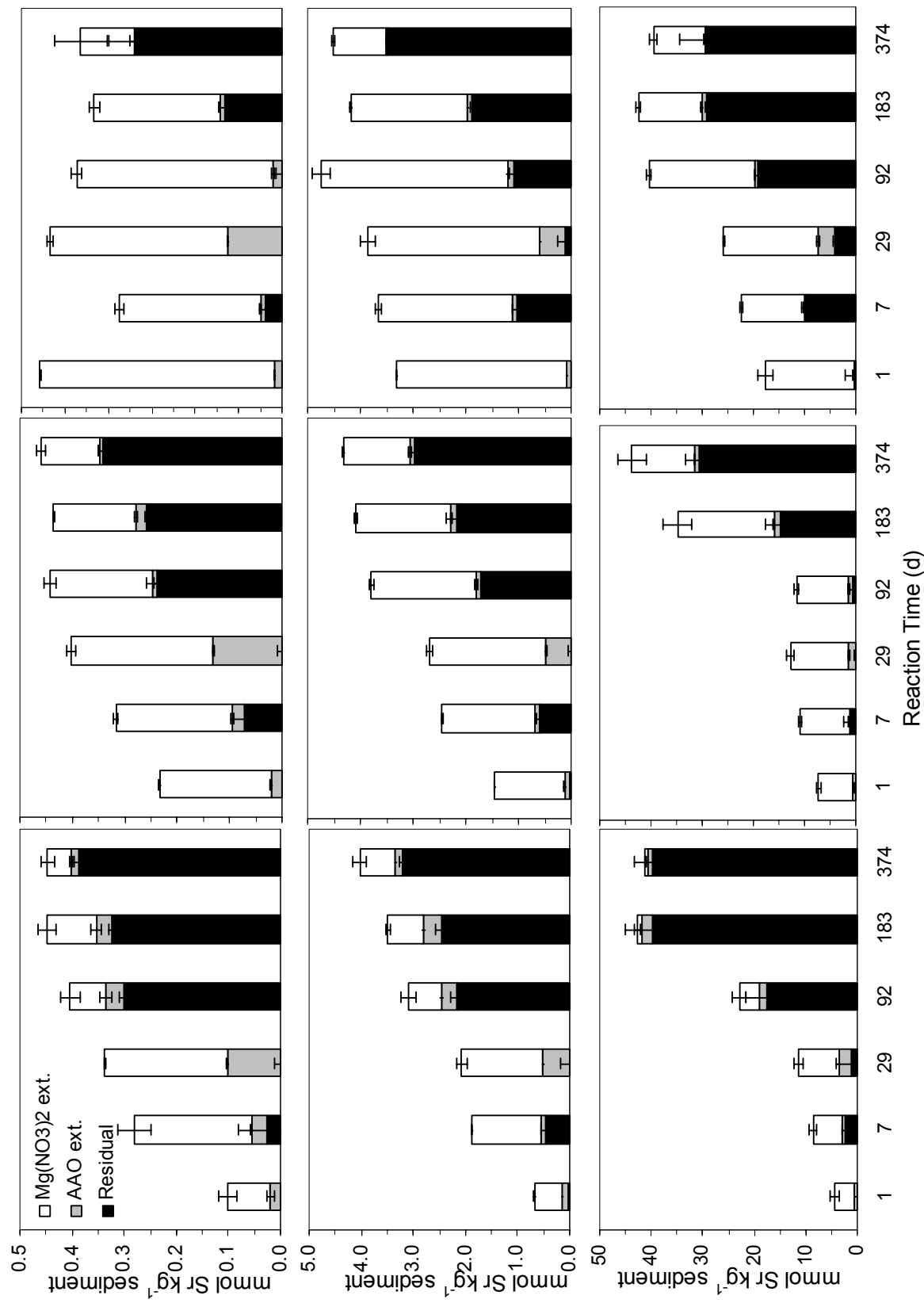


Figure 4. Sr partitioning determined by sequential extractions of HC, HF, RS sediments following reaction with STWL for 1 to 374 d. Initial Cs and Sr concentrations of (a) 10⁻⁵ M; (b) 10⁻⁴ M; (c) 10⁻³ M. Left to right: HC, HF, RS.

NMR Spectroscopy:

For the weathered kaolinite systems studied in this collaborative research, solid-state ^{27}Al magic-angle spinning (MAS) NMR experiments at variable magnetic field strength have been reported previously. Changes in line shapes and positions were noted as a function of field, and were correlated with changes in x-ray patterns and other spectroscopic and analytical data (see Chorover *et al.* 2003). To better resolve the ^{27}Al NMR resonances from these systems, it was necessary to acquire data at higher magnetic field strengths. In two trips to the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratories (PNNL), we utilized 17.3 T and 18.8 T NMR spectrometers for measurements of ^{27}Al MAS and multiple-quantum MAS (MQMAS) spectra from a suite of weathered kaolinite and montmorillonite clays. Samples run during the first visit in November 2002 included an unweathered kaolinite sample and three time series of weathered kaolinite samples (12 samples - from 30 days up to 369 days of contact with simulated tank waste leachates with three different initial concentrations of cesium and strontium). All three 90-day and 369-day weathered samples were also investigated after acidic oxalate treatment (6 samples) to remove poorly crystalline material. In May 2003, time allotted on the 18.8 T instrument was used to investigate two kaolinite samples (365 day treatments at two initial concentrations of cesium and strontium) and thirteen additional montmorillonite samples treated similarly to the kaolinite samples. During this second visit, ^{23}Na MAS data were also obtained from twelve reacted samples, and ^{27}Al MQMAS data were acquired from select systems.

The superior resolution obtained at higher magnetic field strengths is exemplified in the spectra of Figure 1, where a reacted kaolinite sample (190-day treatment) was probed as a function of magnetic field strength. Results from the variable-field NMR measurements are now being analyzed for calculation of relative amounts of each neoformed species present, as well as calculation of isotropic chemical shift and quadrupolar parameters. These experimentally-determined NMR parameters are structure-dependent, and can be utilized as fingerprints for phase identification (Crosson *et al.*, 2003, *in prep*).

MQMAS experiments provide greater spectral resolution and (often) more precise measurement of NMR parameters, and therefore a set of samples (including the 369-day reacted kaolinite samples) have also been analyzed at EMSL with MQMAS. In the spectrum of Figure 2, four discernable peaks appear for this sample and analysis of their spectral frequencies in two dimensions will provide the quadrupolar and chemical shift parameter values, as well as a measure of any distribution of parameters in amorphous or poorly crystalline phases. Full analysis of these data will lead to a publication and form a component of the thesis of graduate student Garry Crosson.

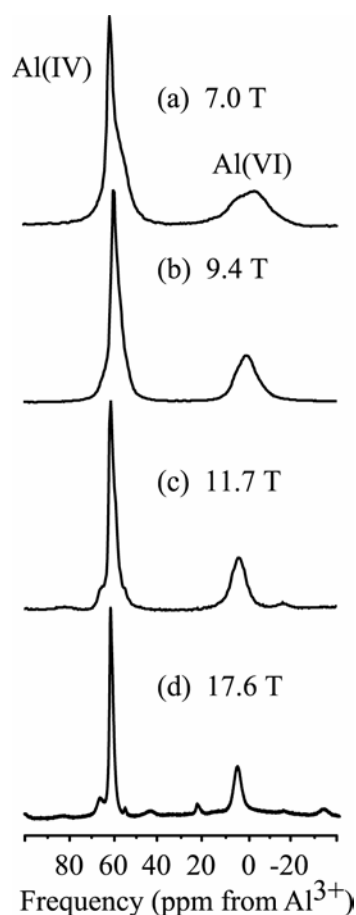


Figure 5: Multiple-field ^{27}Al MAS spectra, as described in text.

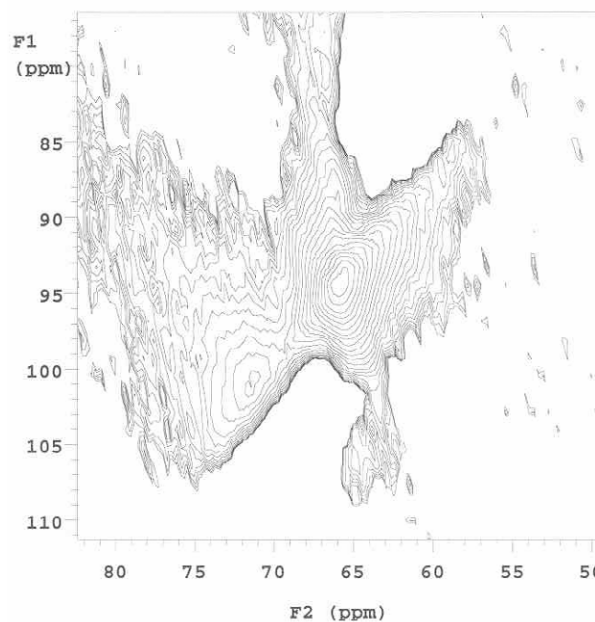


Figure 6: ^{27}Al MQMAS spectrum of a weathered kaolinite sample, displaying resolution of resonances from different aluminum environments.

To complete the studies of weathered kaolinite systems, ^{23}Na single-pulse MAS and ^{23}Na MQMAS experiments will be performed on select samples to resolve and identify multiple sodium sites observed in previous high-field studies. These experiments will be carried out on the Penn State University 500 MHz NMR system. Additionally, ^{27}Al MAS, ^{27}Al MQMAS (at 500 MHz) and ^{29}Si MAS experiments will be performed on weathered montmorillonite specimens, and the relevant NMR parameters and the speciation for aluminum and silicon will be determined and evaluated as a function of contact time with the synthetic waste leachate.

Presentations, Publications and Theses

Presentations

- Crosson, G. 2003. Incongruent dissolution reactions of kaolinite in synthetic tank waste leachate solutions: Solid-state NMR studies. Department of Chemistry, George Mason University, Fairfax, Virginia, 30 January 2003.
- Chorover, J. 2003. 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.
- Crosson, G. 2003. " ^{27}Al and ^{29}Si Solid-State Nuclear Magnetic Resonance Characterization and Quantification of Newly Formed Aluminum Containing Phases in Weathered Kaolinite Clay Systems", talk by G. S. Crosson at the *National Organization for the Professional Advancement of Black Chemists and Chemical Engineers: Annual Conference*, Indianapolis, Indiana, 13-17 April 2003.

- Chorover, J. 2002. Coupled weathering and contaminant uptake in Hanford sediments. Department of Environmental Science Seminar Series, University of California at Riverside. April 2002.
- Mueller, K. T. 2002. Structural and chemical studies of complex materials using solid-state NMR spectroscopy. Chemistry Department Seminar Series, Arizona State University, Tempe, Arizona, 27 September 2002.
- Crosson, G. and K. T. Mueller. 2002. Solid-State NMR studies of aluminosilicate formation in weathered clay systems, poster presented at *Federation of Analytical Chemistry and Spectroscopy Societies 29th Annual Meeting*, Providence, Rhode Island, 13-17 October 2002.

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., A. Vairavamurthy, K. G. Karthikeyan, and J. Chorover. 2002. Cesium adsorption on clay minerals: An EXAFS spectroscopic investigation. *Environmental Science and Technology*, **36**, 2670-2676.
- 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.
- 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
- Serne RJ, HT Schaef, BN Bjornstad, DC Lanigan, GW Gee, CW Lindenmeier, RE Clayton, VL LeGore, MJ O'Hara, CF Brown, RD Orr, GV Last, IV Kutnyakov, DS Burke, TC Wilson, and BA Williams. 2002. *Geologic and geochemical data collected from vadose zone sediments from Borehole 299 W23-19 [SX-115] in the S/SX Waste Management Area and preliminary interpretations*. PNNL-13757-2, Pacific Northwest National Laboratory, Richland, Washington.
- 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. *Geologic 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. *Geologic 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.*