ANNUAL PROGRESS REPORT

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Project Title: **Interfacial Soil Chemistry of Radionuclides in the Unsaturated Zone**
Lead Principal Investigator: Dr. Jon Chorover, The Pennsylvania State University, Soil Science Program, 116 ASI Building, University Park, PA 16802: Tel (814) 863-5394; Email: jdc7@psu.edu
Co-Investigators: Dr. Karl T. Mueller, The Pennsylvania State University, Department of Chemistry, 152 Davey Laboratory, University Park, PA 16802; Tel: (814) 863-8674; Email: ktm2@psu.edu
Dr. K. G. Karthikeyan, Department of Biological System Engineering, University of Wisconsin, Madison, WI 53706; Tel: (608) 262-9367; Email: kkarthikeyan@facstaff.wisc.edu
Dr. A. Vairavamurthy, Brookhaven National Laboratory, Department of Applied Science, Building 815, Upton, New York 11973; Tel: (516) 344-5337; Email: vmurthy@bnl.gov
Mr. R. Jeff Serne, Pacific Northwest National Laboratory, Applied Geology & Geochemistry Group, Richland, WA 99352; Tel: (509) 376-8429; Email: Jeff.serne@pnl.gov
Graduate Students: 2 [Garry Crosson; Paula Rotenberg]
Postdoctoral Scholar: Sunkyung Choi

SPECIFIC DOE PROBLEMS ADDRESSED BY THE PROJECT

In this project, research integrating kinetic and spectroscopic studies is being conducted to address the contamination problems associated with radionuclides (Cs^{+}/Sr^{2+}) at DOE sites (e.g. Hanford, WA; Savannah River Site, Aiken, SC). The focus is on understanding the interfacial reactions responsible for contaminant sorption and associated immobilization and retardation under relevant geochemical (pH=14; 2M Na^{+} background) conditions. Applications of appropriate remediation technologies require information on the strength of interaction between the contaminants and solid phases. This study will contribute to developing geochemical explanations pertinent to the observed migration characteristics of these contaminants in the vadose zone. The results obtained may be applied to equilibrium and transport models for quantifying radionuclide distribution between solid, colloidal, and dissolved phases. Such models are already in use for predicting future migration of the contaminant plume.

RESEARCH OBJECTIVES

A number of previous studies focused on dissolution and precipitation rates of clay systems in acidic to neutral conditions without the presence of radionuclides (1-5). However, there is lack of information concerning sorption, dissolution and precipitation kinetics of clays at high pH and ionic strength with radionuclides present, which is representative of the actual conditions in the study area. We are focusing on the behavior of clays and sediments under these geochemical conditions by: i) investigating dynamics of Cs and Sr uptake over time during the reaction of synthetic tank waste leachate (STWL) with specimen clays and Hanford sediments through batch experiments ii) studying the weathering behavior of clays and Hanford sediments under the extreme geochemical conditions imposed by STWL iii) investigating the dissolution and precipitation behavior of layer silicates using XRD, SEM/EDS, FTIR, TG/DTA, AFM and HRTEM and iv) investigating the surface chemistry and sorption sites of clay minerals using XPS, NMR and XAFS.

RESEARCH PROGRESS and IMPLICATIONS

This report summarizes work after 20 months of a 36 month project.

I. Weathering Behavior and Cs/Sr uptake of Clays under Extreme Geochemical Conditions

1.1 Adsorbed and Released Cs/Sr

Batch experiments were conducted using STWL (0.05 M Al_T, 2 M Na^{+}, 1 M NO_3^{-}, pH ~14) reacted with Na-saturated illite, vermiculite, montmorillonite, and kaolinite. Experiments were conducted for periods ranging from 1 to 190 days (and continuing to longer reaction times), with initial Cs/Sr concentrations of 10^{-5}, 10^{-4} and 10^{-3} M. After fixed reaction times, Cs, Sr, Al, Si, and Fe concentrations are measured in solution and solid phases to determine radionuclide sorption and to study kinetics of clay dissolution and secondary mineral precipitation. Clays are extracted sequentially with $Mg(NO_3)_2$ (0.1 M, pH 7) and acid ammonium oxalate solution (0.2 M, pH 3) to identify Cs and Sr fractions sorbed into "exchangeable" and "poorly-crystalline" (defined operationally) phases.

With respect to Cs sorption, most clays sorbed more Cs as aging time increased (data not shown). At the lower initial concentration, preferential sorption of Cs by illite is observed. Illite is known to comprise high-affinity, frayed-edge sites that are highly selective for Cs (6). Results of $Mg(NO_3)_2$ and acid ammonium oxalate (AAO) extractions shows that large quantities of Cs exist in the residual solid phase (i.e. nonextractable form), and that this fraction increases with time (i.e., increasing recalcitrance of Cs). Figure 1 shows adsorbed and released amounts of Sr in each clay during the 190 day reaction time at the 10^{-5} M Cs/Sr concentration.

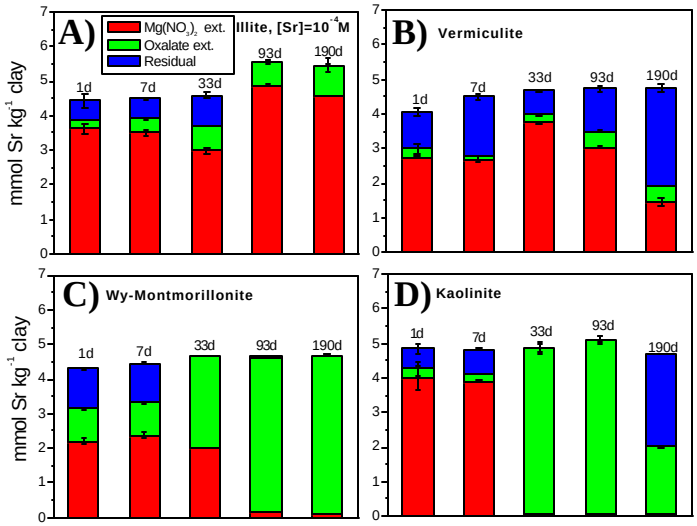

Fig. 1. Sorption of Sr in illite, vermiculite, montmorillonite and kaolinite suspensions in contact with STWL for 1 to 190 days (initial Sr = 10^{-4}M). The full height of each bar indicates the total amount sorbed, and the different colors represent the amount extracted by $Mg(NO_3)_2$ (ion exchangeable), ammonium oxalate (poorly crystalline solids) and the residual portion (non-extractable).

In particular, the amount of Sr extracted by AAO over time in montmorillonite and kaolinite directly track the formation of *secondary minerals* (defined as solid phase products in any given suspension reaction). Some secondary phases are detected by XRD in montmorillonite and kaolinite after 33 days of reaction time. At early times, secondary precipitates may be poorly crystallized and easily degraded by AAO. However, with prolonged aging, crystallinity is increased and AAO extractability is reduced. For example, secondary products of the kaolinite reaction are less extractable after 190 days of contact with STWL. Dissolution of Si leads to the precipitation of zeolites and short-range-ordered Al and Si phases that impact the kinetics of Cs and Sr uptake (Fig. 2). The time-dependency of aqueous Si concentrations show effects of secondary mineral precipitation.

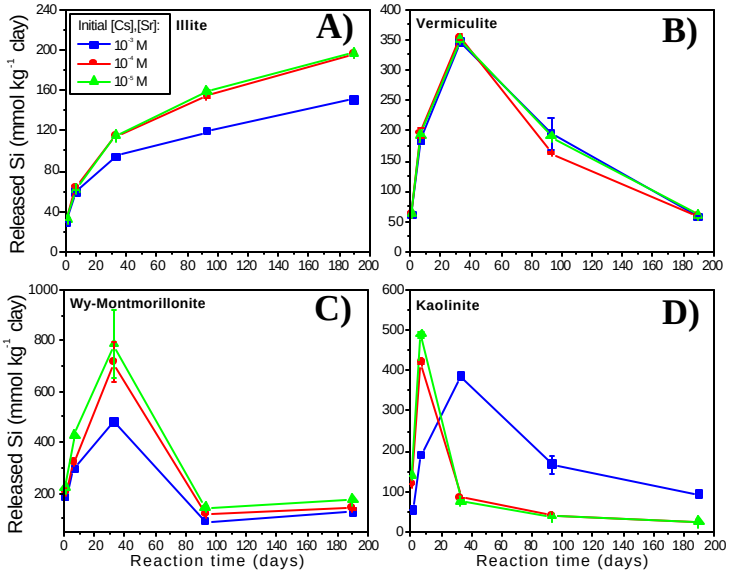

Fig. 2. Dissolution of Si over the 190 d reaction time with STWL.

The increase and subsequent decrease in aqueous Si concentration corresponds with clay dissolution and secondary phase formation, respectively, as observed by XRD, FTIR and SEM/EDS. Interestingly, initial Cs/Sr concentrations controlled the kinetics and pathways of solid phase transformation.

1.2 Mineralogical Changes Over the Course of Dissolution

Effects of OH^- promoted weathering processes (dissolution and precipitation reactions) depend on the initial Cs/Sr concentration and type of clay. Figure 3 shows secondary zeolites formed in kaolinite and montmorillonite suspensions at different initial Cs/Sr concentration following 190 days of reaction. Na-Al-NO_3 silicate-containing zeolite is a common secondary mineral formed in kaolinite and montmorillonite suspensions.

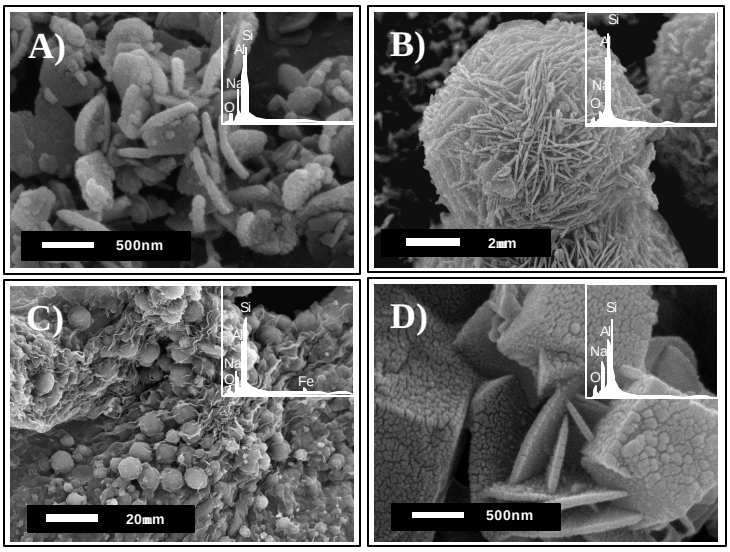

Fig. 3. SEM images showing secondary phase formation after 190 days in kaolinite (A, B) and montmorillonite (C, D) suspensions at 10^{-5} M and 10^{-3} M Cs/Sr. SEM/EDS spectra indicate Na-containing containing zeolites.

X-ray image mapping with SEM clearly shows uptake of Sr in secondary precipitates (data not shown). Investigations with FTIR (DRIFT), TGA and TEM provide additional confirmation of the kinetic data. The rate of secondary precipitation formation was greatest for kaolinite followed by montmorillonite, vermiculite and illite.

1.3 Solid-State MAS ^{27}Al NMR studies

Solid-State magic angle spinning (MAS) ^{27}Al NMR studies have been conducted on weathered kaolinite at varied STWL contact times (up to 190 days) over a range of Cs/Sr levels (10^{-3}, 10^{-4} and 10^{-5} M). NMR results are shown in Figure 4. The unreacted sample shows a broad resonance from octahedrally coordinated aluminum, typical of kaolinite. During the reaction, emergence of new peak(s) are observed in the asymmetric resonance near 50-65 ppm. This spectral change indicates the formation of new phases containing tetrahedral aluminum sites. XRD studies of kaolinite are consistent with NMR results, and show the formation of cancrinite (sodium aluminum nitrate silicate zeolite) and chabazite (strontium silicate hydrate zeolite), which contain tetrahedral Al. Over the range of Cs/Sr concentrations studies, it has been observed that the contaminant concentration affects the rate at which new tetrahedral aluminum phases are formed in the system. In addition to these initial ^{27}Al NMR experiments, we performed ^{27}Al NMR studies on ammonium oxalate treated samples.

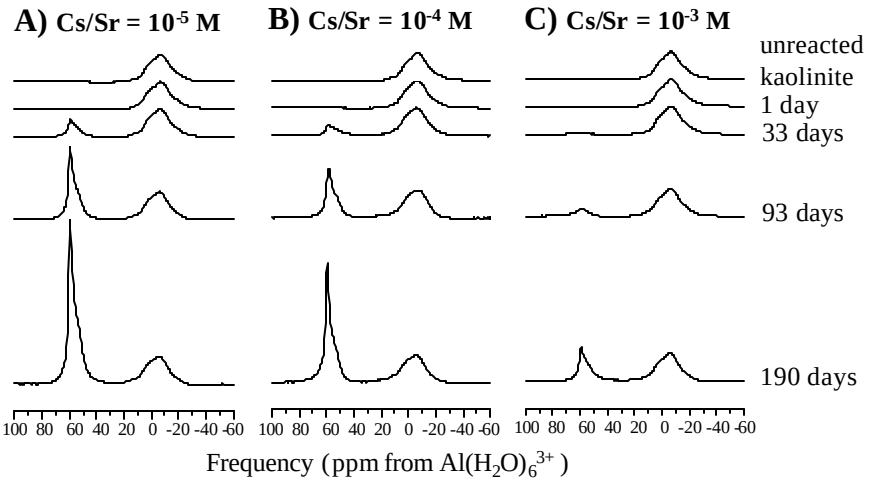

Fig. 4. The ^{27}Al MAS NMR spectra of kaolinite treated with STWL containing A) 10^{-3} M, B) 10^{-4}M and C) 10^{-5}M of Cs/Sr with reaction time up to 190 days.

Overall, the rate of solid product formation was greatest for kaolinite, followed by montmorillonite, vermiculite and illite. The results indicate that the extent of radionuclide immoblization depends strongly on the nature of reactant minerals.

II. Cs/Sr uptake and Mineralogical Changes of Hanford sediments

Uncontaminated sediments from Hanford were reacted with STWL in order to determine how i) Cs and Sr sorption and ii) mineral transformations of sediments were affected by intense geochemical conditions comparable to those at Hanford, WA. Sediments were freeze dried and examined by x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM/EDS) to characterize mineral composition and alteration.

Significant Cs and Sr sorption occurred, despite conditions of high ionic strength and the presence of 2 M Na^+ as a competing cation. Cs and Sr sorption generally increased over time (data not shown). After 183 days, up to 33% of all initial Cs and 100% of initial Sr added were retained in the solid phase. Considerably more Sr uptake occurred than Cs for all sediment types and loadings. However, a higher proportion of Cs remained bound to sediments following sequential extractions after reaction times of up to 30 days. This suggests that after shorter reaction periods, Sr is more easily removed *via* ion exchange and dissolution of oxalate extractable materials than is Cs. However, after 183 days, a large proportion of Sr remains sorbed to the sediment, thus demonstrating the importance of reaction kinetics. SEM/EDS shows secondary mineral phases in Ringold silt and Hanford sediment after 183 days (Fig. 5).

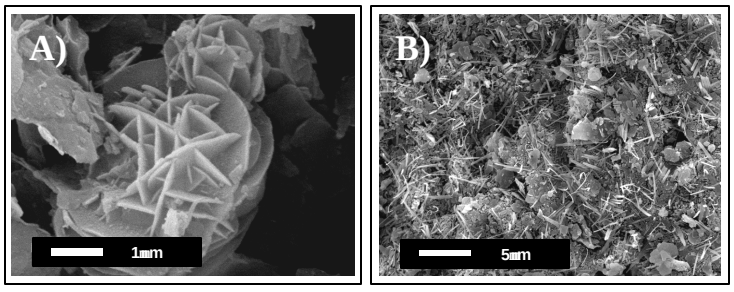

Fig. 5. SEM images showing neoformed solid phases after 183 days in (A) Ringold Silt and (B) Hanford Fine sediments at a contaminant loading of 10^{-3} M Cs/Sr.

V. PLANNED ACTIVITIES

Macroscopic experiments involving Cs^+ and Sr^{2+} sorption to specimen clay minerals and Hanford sediments (Hanford coarse, Hanford fine and Ringold silt) in the presence of STWL will be continued as a function of time (1 year and 2 years) to determine the rate of sorption and investigate the weathering effects under Hanford-specific conditions. Also, Cs^+ and Sr^{2+} desorption kinetics will be evaluated on clay and Hanford sediments systems [time frame: next 15 months]. For a better understanding of preferential Cs^+ and Sr^{2+} sorption sites and surface chemistry of clay minerals, HRTEM, HRXRD, XPS and XAFS are will be used [time frame: next 15months].

Additional ^{27}Al NMR experiments will be employed to monitor the evolution with time of the asymmetrical absorption for kaolinite subjected to STWL solutions. Furthermore, we will attempt to conclusively identify the chemical species associated with this feature using ^{27}Al NMR multiple quantum MAS techniques. ^{29}Si NMR experiments will also be employed to monitor changes in the silicon environments over the course of time with possible quantification of the Si/Al ratio in new mineral phases based on a combination of ^{29}Si and ^{27}Al NMR. In addition, we have proposed ^{133}Cs NMR studies to follow changes in the chemical environment of cesium over time within reacted clays. ^{133}Cs NMR studies of weathered kaolinite will provide information on the nature of sorption sites, cesium location, and relative mobility of cesium within this weathered environment [time frame: next 15 months].

Thermodynamic studies of Na-Sr, Na-Cs exchange reactions in montmorillonite and vermiculite will be investigated at high pH. The present study will clarify the cation-mixing properties in montmorillonite and vermiculite by applying a statistical thermodynamic theory to cation-exchange equilibria [time frame: next 15months]. This study will employ DTA, DSC, HRTEM and HRXRD will be used.

References:

(1) Bauer A. and Berger G. (1998) Kaolinite and smectite dissolution rate in high molar KOH solutions at 35°C and 80°C, Appl. Geochem. 13:905-916.

(2) Bauer A. and Velde B. (1999) Smectite transformation in high molar KOH solutions, Clay Minerals, 34:259-273.

(3) Cama J., Ganor J., Ayora C., and Lasaga A. C. (2000) Smectite dissolution kinetics at 80°C and pH8.8, Geochim. Cosmochim. Acta 64:2701-2717.

(4) Devidal J. L., Schott J., and Dandurand J. L. (1997) An experimental study of kaolinite dissolution and precipitation kinetics as a function of chemical affinity and solution composition at 150 °C, 40 bars, and pH 2, 6.8, and 7.8, Geochim. Cosmochim Acta 61:5165-5186.

(5) Sutheimer S. H., Maurice P. A., and Zhou Q. (1999) Dissolution of well and poorly crystallized kaolinites: Al speciation and effects of surface characteristics, Am. Min. 84:620-628.

(6) Comans, R N. J., Haller, M., and P. De Preter. (1991) Sorption of cesium on illite-equilibrium behavior and reversibility. Geochim. Cosmochim. Acta 55:433-440.