Interfacial Soil Chemistry of Radionuclides in the Unsaturated Zone

Project ID: 70126

Dr. Jon D. Chorover, The Pennsylvania State University

Dr. Karl T. Mueller, The Pennsylvania State University
Dr. K.G. Karthikeyan, The Pennsylvania State University
Dr. A. Vairavamurthy, Brookhaven National Laboratory
R. Jeff Serne, Pacific Northwest National Laboratory

Research Objectives

In this project, basic research integrating macroscopic and spectroscopic studies are 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; 3 M Na^+ background) conditions. Application of appropriate clean-up technologies requires information on the strength of interaction between the contaminants and solid phases. This study will provide suitable geochemical explanation pertinent to the observed migration characteristics of these contaminants in the vadose zone. The results obtained will find applications in 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.

The main objectives of this work are to: i) quantify the rate and extent of radionuclide sorption/desorption on pristine and altered clay surfaces through macroscopic batch and column experiments, ii) investigate dissolution behavior of layer silicates induced by these extreme geochemical conditions using XRD, FTIR, and NMR spectroscopies, and iii) identify the mechanisms of interaction at the molecular level using NMR and XAS spectroscopies.

Research Progress

This report summarizes work after 4.5 months of a 3-year project.

Preparation and Characterization of Clay Minerals

Specimen clay minerals Georgia kaolinite (KGa-2), Wyoming montmorillonite (SWy-2) and Silver Hill illite (IMt-1) were acquired from the Source Clay Minerals Repository at the University of Missouri, and vermiculite from Ward's, NY. The < 2μm size fraction of kaolinite and montmorillonite were collected by dispersion, sedimentation and centrifugation, and the clays were treated to remove surficial metal, oxide and organic impurities prior to repeated homoionic saturation in NaCl solution. Illite and vermiculite were fractionated gravimetrically to obtain a fraction < 115μm, purified and Na-saturated as mentioned above. The clay minerals are stored in aqueous suspension prior to use. The clay minerals have been characterized using solid-state ^{27}Al and ^{29}Si CPMAS NMR spectroscopy.

Sorption Experiments

Preliminary experiments were conducted to determine Cs^+ sorption capacity and $Na^+ \rightarrow Cs^+$ selectivity of the clay minerals as well as ascertain the detection limits of NMR and XAS spectroscopies. Cs-saturation of clay minerals was achieved by equilibrating once with 0.5 M CsCl

[1h], twice with 0.1 M CsCl [1h], and once with 0.05 M CsCl [8d]. Cs-saturated clays were then reacted twice with 0.01 M NaCl to displace Cs^+ from sites with lower $Na^+ \rightarrow Cs^+$ selectivity. A final washing step with 1.0 M NH_4OAc extracted Cs^+ from sites exhibiting highest $Na^+ \rightarrow Cs^+$ selectivity. Table 1 provides the total Cs^+ sorption capacity of the clay minerals and surface excess values after successive NaCl extractions. Highest sorption capacity was observed for montmorillonite followed by vermiculite, illite, and kaolinite. The data in Table 1 indicate that Cs^+ continues to desorb from clay mineral surfaces with increasing NaCl exchange steps. These samples are being analyzed by NMR and XAS spectroscopies to elucidate the local structural environment. To closely simulate the characteristics of REDOX/PUREX waste streams at Hanford, synthetic waste liquor [SWL] with the following composition (Al - 0.1 M; Na^+ - 3 M; NO_3^- - 1.2 M; NO_2^- - 0.9 M; pH^a~14) has been prepared for use in subsequent experiments.

NMR spectroscopy

Solid-state NMR experiments are vital for understanding the local environments of the cations of interest in relation to the framework structure of the clay mineral. Montmorillonite is of interest due to its ability to selectively encapsulate species such as Cs^+ and Sr^{2+}. The structure of montmorillonite is complex and the ^{29}Si MAS spectrum (Fig. 1) results in many overlapping lines. Through the use of double- and triple-resonance solid-state NMR experiments, we are able to focus on specific regions within the montmorillonite structure and identify the type of framework position and cation that is present. Preliminary cross-polarization (CP) experiments involving the transfer of polarization from protons to Si have been performed. Using kaolinite and a hydrated Na-A zeolite as standards, we have been studying the difference in CP from surface hydroxyls compared to water molecules as a function of the contact time used for polarization transfer. The same experiments on montmorillonite with a short contact time (polarization mainly from surface hydroxyls, Fig. 2) and a long contact time (polarization mainly from water molecules, Fig. 3) show differences in the Si spectrum.

Planned Activities

Macroscopic batch experiments involving Cs^+ and Sr^{2+} sorption to specimen clay minerals contacting SWL are being performed as a function of time [1d, 7d, 1-30 months] to determine the rate and extent of radionuclide sorption under Hanford-specific conditions. Dissolution of clay minerals is monitored through measurements of soluble Al/Si and using XRD, FTIR and NMR spectroscopies. These sorption experiments will be extended to uncontaminated sediments obtained from Hanford [Time frame: next 6 months]

TRAPDOR and TEDOR experiments are being developed which will allow for identification of the relationship of Na and Cs cations with the tetrahedral and octahedral Al atoms and the Si atoms of the clay mineral framework. We are pursuing TRAPDOR measurements that will utilize the selective excitations effects of the CP experiments. The excitation is followed by the determination of proximities of the excited species to the Na and Cs cations, to identify whether the cations are near frayed edge sites (Si atoms with hydroxyl groups) or on the basal surface. Planned studies will investigate saturated samples and those subjected to successive extractions [Time frame: next 6-9 months].

X-ray absorption spectra at the Cs L-edge and Sr K-edge for the samples generated from macroscopic experiments will be collected at the bending magnet beam lines X18B at NSLS, Brookhaven National Laboratory. XAS data will help elucidate the coordination environment of the sorbed Cs^+ and Sr^{2+}, the modes of interaction, and the type of sorption complex formed [Time frame: next 6-9 months].

Table 1. Cs^+ sorption capacity and surface excess (q_{Cs}) following repeated extractions with 0.01 M NaCl.

Clay Mineral	Sorption capacity [$mmol_c\ kg^{-1}$]	q_{Cs} [$mmol_c\ kg^{-1}$] 1	2
Kaolinite	36.43±1.87	12.90±3.2	8.55±0.77
Montmorillonite	783.37±0.63	626.73±5.22	538.50±7.23
Illite	150.58±2.87	90.30±2.15	67.96±0.73
Vermiculite	271.00±6.80	190.92±2.04	158.94±1.48

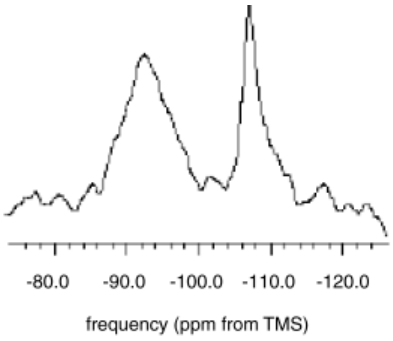

Figure 1. ^{29}Si MAS spectrum of Montmorillonite.

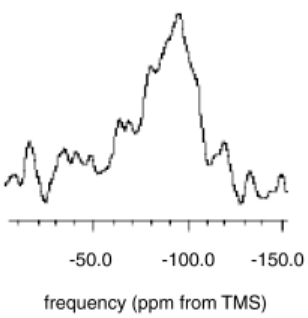

Figure 2. ^{29}Si CP MAS spectrum of Montmorillonite (contact time = 2.5 ms).

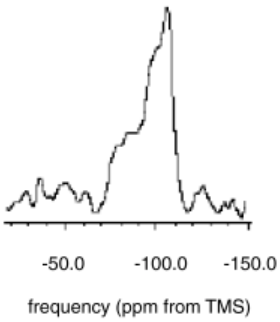

Figure 3. ^{29}Si CP MAS spectrum of Montmorillonite (contact time = 12 ms).