INTERACTION OF Cs AND Sr WITH SPECIMEN CLAYS IN THE PRESENCE OF TANK WASTE LEACHATE

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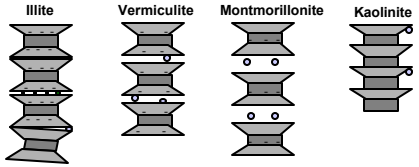
EXPERIMENTAL

Specimen clays used in this study



I. Preparation and Characterization of Clays

i) Source:

Georgia kaolinite (KGa-2)	Source Clay Minerals Repository Univ. Missouri
Wyoming montmorillonite (SWy-2)	
Silver Hill illite (IMt-1)	
Vermiculite	Ward's, NY

ii) Preparation:
Kaolinite & Montmorillonite: < 2 μm size fraction collected by dispersion, sedimentation and centrifugation. Clays treated to remove surficial metal, oxide and organic impurities, and Na-saturated.

Illite & Vermiculite: < 115 μm fractionated gravimetrically, purified and Na-saturated.

II. Macroscopic Sorption Experiments

i) Cs-saturation studies:
Initial studies to determine Cs^+ sorption capacity and Na^+ ® Cs^+ selectivity of clay minerals
Cs-saturation 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 washed with 0.01 M NaCl to displace Cs^+ from sites with lower Na^+ ® Cs^+ selectivity. Final washing with 1M NH_4OAc to extract Cs^+ from sites with highest Na^+ ® Cs^+ selectivity.

ii) Hanford-specific geochemical conditions:
Investigate sorption of Cs^+/Sr^{2+} to clays at high pH and background $Al(OH)_4^-$ and Na^+ levels.
Synthetic Tank Waste Leachate [STWL] prepared to closely simulate REDOX/PUREX waste streams [Al_T-0.1 M; Na^+-2.2 M; NO_3^--1.2 M; NO_2^--0.9 M; pH » 13]

Specimen clays (10 g/L) were reacted with STWL for desired equilibration [1, 7d] at initial Cs/Sr concentrations of 0.01 M and $5x10^{-6}$ M. After reaction, suspensions were centrifuged and filtered [0.2 μm]. Soluble Cs, Sr, Al, and Si were measured by AA [flame & GFAA] to determine the extent of radionuclide sorption and monitor clay weathering. pH was measured using AccuFET solid-state pH electrode. The solids were washed with ethanol to remove entrained salts and air-dried prior to XRD, FTIR, and NMR analyses.

III. Spectroscopic Investigations

Clay dissolution and formation of new Al(hydr)oxides, alumino-silicate solid phases were monitored using XRD, DRIFT, and NMR spectroscopies.

- Nature of Cs sorption sites [in relation to neighboring Al and Si atoms] are being probed by NMR techniques such as cross polarization (CP), rotational echo double resonance (REDOR) and transfer of populations by double resonance (TRAPDOR).
- Changes in the local molecular environment of Cs and Sr due to reactions with STWL are being investigated by XAS.

i) Nuclear Magnetic Resonance (NMR) :
^{27}Al and ^{29}Si NMR spectra were collected on a 400 MHz spectrometer with ^{27}Al at 104.4 MHz and ^{29}Si at 79.4 MHz.

ii) X-ray Diffraction (XRD):
XRD analysis on Na-sat. clays and clays reacted with STWL was conducted on a Syntag Vax 310 system using Cu-Kα radiation.

iii) X-ray Absorption Spectroscopy:
Experiments conducted on beamline X19A at the National Synchrotron Light Source, Brookhaven National Laboratory. XAS data were collected at the Cs L-edge. Analysis of data were performed using UWXAFS program and FEFF7 simulations.

RESULTS

I. Macroscopic Sorption Experiments:

i) Cs-saturation studies:
Table 1 provides the total Cs^+ sorption capacity of the clays and the surface excess after successive Na^+ 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 with increasing Na^+ exchange steps.

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

Clay	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

ii) Hanford-specific geochemical conditions:
Figures 1-2 illustrate the effect of STWL in controlling the *sorption* (*defined here as uptake from solution*) of Cs and Sr to the solid phase.

Cs Sorption: The extent of removal is significantly lower than the sorption capacity of the clays indicating competitive effects from Na^+, Sr^{2+}, and potential blocking of Cs^+ sorption sites by the secondary Al solid phases. Some common trends are observed for all clays (except illite at the lower initial concentration):
a) increasing contact time decreases the amount of Cs sorbed,
b) minor differences between the clays and control were observed, indicating the importance of the STWL in controlling Cs sorption.
At the lower initial concentration, *preferential sorption* of Cs by illite is observed. Illite is known to contain high affinity frayed edge sites [FES] that are highly selective for Cs [1].

Sr Sorption: At the lower initial concentration, complete uptake occurs [except for illite]. Vermiculite exhibits a *high affinity* for Sr even at the higher initial Sr concentration. A slight decrease in the amount sorbed is seen with increasing contact time. Extent of Sr sorption [$mmol\ kg^{-1}$] is higher than that of Cs.

Figure 1. Cs Interaction with Clays

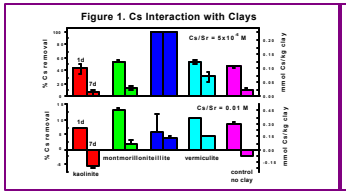
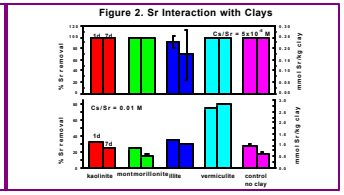


Figure 2. Sr Interaction with Clays



Figures 3 and 4 show the soluble Al and Si data for the clays-STWL contact experiments. The initial contaminant concentration influences the amount of soluble Si and Al present at each sampling time: higher Al and lower Si levels are observed at higher initial Cs & Sr. The Al concentrations decrease marginally with increasing reaction time and the opposite is true for Si. Presence of a dynamic dissolution-reprecipitation regime in these systems makes it difficult to assess the source of soluble Al [clay dissolution vs. initial Al addition] and also determine the extent of clay weathering based on the Si levels.

Figure 3. Dissolved Al

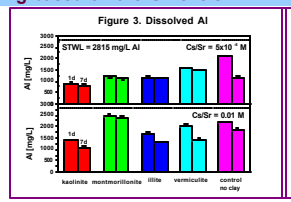
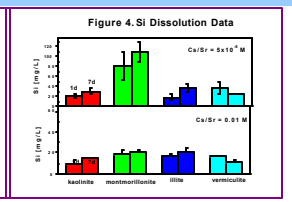


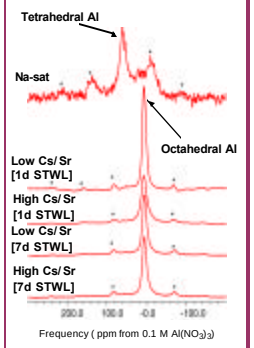
Figure 4. Si Dissolution Data



II. Spectroscopic Investigations:

i) NMR Studies:
^{27}Al and ^{29}Si MAS NMR analyses help monitor the dissolution-reprecipitation processes occurring in these systems. Figures 5 and 6 contain the ^{27}Al and ^{29}Si NMR data for vermiculite and illite, respectively, as a function of different treatments [i.e., equilibration time and contaminant concentrations]. In the presence of STWL, irrespective of the treatment, disappearance of the tetrahedral Al peak [62 ppm in the Na-sat. vermiculite and 54.5 ppm for Na-sat. illite] and increase in intensity of the octahedral Al peak [6-10 ppm] are observed. The ^{29}Si NMR spectra of illite [Fig. 7] are complex and show no dramatic changes as a result of reaction with STWL. Upcoming $^{29}Si/^{27}Al$ and $^{1}H/^{29}Si/^{27}Al$ connectivity experiments will help to selectively edit the ^{29}Si NMR spectra to identify the relationship between Al, Si, and OH and determine if any secondary SRO aluminosilicates [e.g., allophanes, imogolites] are formed in these systems. Similar Si spectra were also obtained for all the other clays.

Figure 5. ^{27}Al MAS spectra of vermiculite.



*denotes spinning side band

Figure 6. ^{27}Al MAS spectra of illite.

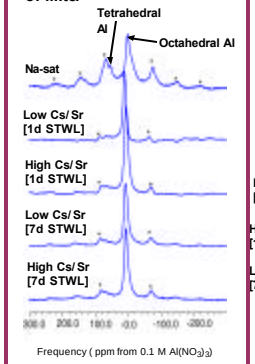
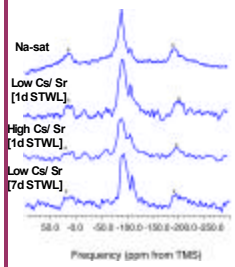


Figure 7. ^{29}Si MAS spectra of illite.



BACKGROUND

Circumneutral Inceptisols

- Smectite
- Vermiculite
- Illite
- Feldspars, Micas

Vadose Zone Contamination at Hanford:

Neutralization of alkaline waste

- dissolution of soil minerals
- release/polymerization of Si
  - $SiO(OH)_3^-$, $Si_4O_6(OH)_6^{2-}$, $SiO_2(OH)_2^{2-}$
- co-precipitation with Al

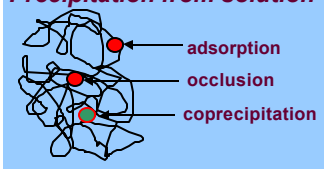
e.g.,

$Al(OH)_4^- + 0.5\ SiO(OH)_3^- + 1.5\ H^+ \rightleftharpoons 0.5(HO)_3Al_2O_3SiOH\ (s) + 2.5\ H_2O$

Precipitation of Al hydroxides, carbonates, and metastable SRO Al/Si phases

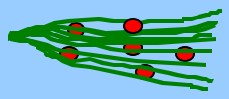
Effects of secondary precipitates on ^{137}Cs and ^{90}Sr:

Precipitation from solution



- High specific surface (300-1000 $m^2\ g^{-1}$)
- Colloidal (5-500 nm)
- Mobile in the vadose zone?

Precipitation on 2:1 layer silicates



- high Cs affinity
- slow kinetics
- low reversibility
- high K_d, K_{ex}

- low Cs affinity
- fast kinetics
- high reversibility
- low K_d, K_{ex}

Sediment Contamination at Savannah River Site:

- Leakage of fuel rods
- High ^{137}Cs and ^{90}Sr in sediments
- High NH_4^+ and K^+ and sediment organic matter (30%)
- Soil mineralogy – kaolinite, illite, HIV, gibbsite, hydrous oxides

SPECIFIC DOE PROBLEMS ADDRESSED

- Contamination problems associated with Cs^+/Sr^{2+} at DOE sites [e.g., Hanford, WA; Savannah River Site, Aiken, SC]

- Understand the interfacial reactions responsible for contaminant sorption and associated immobilization/retardation under site-specific conditions [e.g., pH » 14; 3 M Na^+ background]

OBJECTIVES

1) Quantify the rate and extent of Cs and Sr sorption/desorption on pristine and altered clay surfaces through macroscopic and batch column experiments.

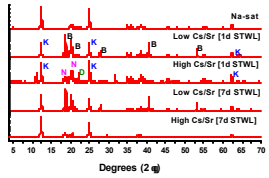
2) Investigate dissolution behavior of layer silicates induced by these extreme geochemical conditions using XRD, DRIFT, and NMR spectroscopies.

3) Identify the mechanisms of interaction at the molecular level using NMR and XAS spectroscopies.

ii) XRD Analysis:

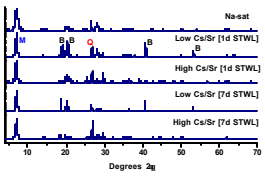
XRD patterns for kaolinite and montmorillonite as a function of different treatments are illustrated in Figures 8 and 9. Precipitation of bayerite [a-$Al(OH)_3$] is clearly indicated in clay-STWL systems at the lower initial Cs/Sr concentrations. The patterns for clays exposed to the higher Cs/Sr levels [except for vermiculite – not shown] did not contain peaks attributable to a particular crystalline Al(hydr)oxide phase.

Figure 8. XRD patterns for kaolinite.



K - kaolinite
B - bayerite
D - diaspore
N - nordstrandite

Figure 9. XRD patterns for montmorillonite.



M - montmorillonite
B - bayerite
Q - quartz

iii) X-ray Absorption Spectroscopy:

XAS data were collected for the samples obtained from the "sorption-capacity" experiments (see section I.i). The Cs L-edge XAS data [radial distribution function uncorrected for phase shift] for montmorillonite, vermiculite [Figures 10 and 11] are shown in comparison to natural zeolites [Figure 12]. Important inferences include:

a) Cs is present in 2 distinguishable chemical environments [more evident in zeolites]
b) Preliminary data fitting indicates that the two major peaks correspond to oxygen
c) Cs with longer bond distance to O (»4.3Å) suggest binding via outersphere complexation [hydrated Cs in the interlayers and bound to edge silanol & aluminol sites]
d) Cs with shorter bond distance to O (» 3.1Å) suggests the formation of inner sphere complexes [most likely Cs sorbed at the siloxane ditrigonal cavities [3].

Figure 10. Sorption of Cs on Montmorillonite: Effect of Loading on the Radial Distribution Function

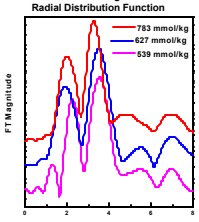


Figure 11. Sorption of Cs on Vermiculite: Effect of Loading on the Radial Distribution Function

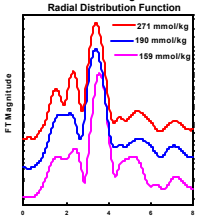
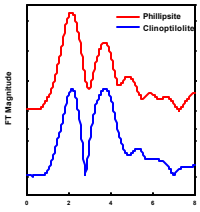


Figure 12. Sorption of Cs on Natural Zeolites



PLANNED ACTIVITIES

I. Macroscopic Sorption Experiments:

i) Effect of reaction time [up to 30 months] on uptake of Cs^+/Sr^{2+} by clays will be evaluated under batch and flow-through column [saturated/unsaturated] conditions.
ii) Sorption experiments will be extended to include uncontaminated Hanford sediments.
iii) Investigate the formation of short range order [SRO] aluminosilicates under homogeneous nucleation conditions and their effects on Cs^+/Sr^{2+} retention.

II. Spectroscopic Studies

i) NMR:

TRAPDOR and REDOR experiments are being developed to facilitate 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 excitation 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. These studies will investigate saturated samples and those subjected to successive extractions.

ii) XAS:

- XAS spectra at the Cs L-edge and Sr K-edge for the samples generated from macroscopic experiments will be collected at BNL.
- Data analysis and theoretical modeling will continue to be performed using the UWXAFS program in conjunction with FEFF7 software to elucidate coordination environments of the sorbed Cs and Sr.

REFERENCES

1. Comans, R.N.J., Haller, M., and P. De Preter. 1991. Sorption of cesium on illite: non-equilibrium behavior and reversibility. *Geochim. Cosmochim. Acta*, 55:433-440.
2. Chapters 7, 10, 12, 13, and 14 in "*Minerals in Soil Environments*," 2nd ed., J. B. Dixon and S. B. Weed (eds.), Soil Science Society of America, Madison, WI, 1989.
3. Sposito, G., *The Surface Chemistry of Soils*, Oxford University Press, NY, 1984.