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CESIUM AND STRONTIUM UPTAKE TO CLAY MINERALS AND THEIR WEATHERING PRODUCTS IN A CAUSTIC WASTE

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INTRODUCTION

Accidental leakage of high level radioactive waste (HLRW) into the subsurface has occurred at several Department of Energy (DOE) sites, including the Hanford Site, WA, the Savannah River Site, GA, and the Oak Ridge Site, TN, because of waste tank overfilling, transfer line breakage and tank failure1. This has resulted in the introduction of highly-caustic, radionuclide-containing solutions into underlying sediments and soils. At the Hanford Site, the bulk of the radioactivity released to the vadose zone is present as ^{137}Cs and ^{90}Sr in concentrations up to parts per million2. As a result of high reactive surface site density and high specific area, clay-sized mineral particles may retard the migration of these radionuclides in receiving sediments *via* adsorption and/or surface precipitation reactions[3]. Although most prior studies have focused on Cs and Sr sorption reactions, the extreme pH (13-14), ionic strength (> 2 M) and Al concentrations (*ca*. 0.01 – 0.2 M) of the HLRW solutions[2,4] are known to favor rapid dissolution of silicates and neoformations of zeolitic and feldspathoid solids on time scales that are relevant to contaminant uptake[5,6].

The fate of radionuclides in this dynamic geochemical environment is poorly understood, but could involve adsorption-desorption on native mineral surfaces, as well as co-precipitation with, or adsorption to, solid-phase products of incongruent dissolution. We have found that Cs and Sr are sequestrated into distinct solid phase products of kaolinite dissolution under those conditions[6]. However, reactions involving

2:1 layer-type silicates, with much higher cation exchange capacity, have not been reported previously. Smectite is the dominant 2:1 layer-type silicate at shallow depths in Hanford soils, whereas illite and vermiculite comtents increase with depth[7]. Thus, there is clear need for experimental data pertaining to the long-term weathering and contaminant sorption behavior of these clay minerals in a caustic aqueous environment. The objective of the present research is to establish linkages between mineral transformation and sorptive uptake of Cs and Sr to layer-type silicates (illite, vermiculite, smectite and kaolinite) and their secondary weathering products during long-term contact with a simulated tank waste leachate (STWL). Here we focus on the 2:1 clay minerals and compare to prior data on kaolinite[6].

MATERIALS AND METHODS

Wyoming montmorillonite (Swy-2) from Crook County, WY, and illite (IMt-1) from Silver Hill, MT, were obtained from the Source Clays Repository of the Clay Minerals Society. Vermiculite was obtained from Ward's Scientific Inc., NY. The < 2 µm montmorillonite fraction was collected by centrifugation and cleaned to remove oxide impurities. The < 115 µm fractions of illite and vermiculite were isolated by sedimentation and then washed on a shaker for 2 hrs with 1.0 mol kg^{-1} NaCl at pH 3. This step was repeated until the pH value of the supernatant solution was also pH 3. The clays were then redispersed and washed repeatedly in 0.01 mol kg^{-1} NaCl adjusted to pH 7 with NaOH until the pH value of the supernatant solution reached pH 6 to 7 before use.

A consistent, CO_2 free background solution (solution concentrations prepared and reported on a mass basis) composed of ultrapure (MilliQ) water with 2.0 mol kg^{-1} Na^+, 1 mol kg^{-1} NO_3^-, 1 mol kg^{-1} OH^- and 0.05 mol kg^{-1} Al_T was prepared to simulate the chemistry of observed tank waste leachate. This STWL was spiked to give three initial aqueous phase Cs^+ and Sr^{2+} concentrations, where each contaminant was added at a level of 10^{-5}, 10^{-4} or 10^{-3} M, and both cations were present in all systems. Batch reactors contained 0.5 g dry mass of clay suspended in 25.0 g of STWL solution. The bottles were placed on an end-over-end shaker at 2 rpm and separate reactors were sampled after 1, 7, 33, 93, 190 and 369 d.

Concentrations of Si, Al, Fe, Cs and Sr in supernatant and acidic ammonium oxalate (AAO) extracts of the clay suspensions were determined by ICP-AES. Changes in clay mineralogy were assessed with powder XRD, infrared spectroscopy and electron microscopy.

RESULTS AND DISCUSSION

The full height of bars in Figure 1, 2 and 3 indicate the number of moles of Cs and Sr sorbed to the solid phase per unit initial mass of clay, whereas the mass fraction of each that is subsequently (i) desorbed by Mg-exchange, (ii) dissolved by AAO extraction or (iii) non-extractable (residual) are differentiated by the stacked bars. The dotted line in each case shows the value for complete removal from solution (*i.e.*, sorbed fraction = 1.0). Uptake of Cs was distinctly different from Sr in all three clay systems. Overall sorptive uptake at the two lower contaminant concentrations (10^{-5} and 10^{-4} M) increased in the order of montmorillonite < vermiculite < illite, whereas vermiculite exhibited higher

Cs sorption at the highest contaminant loading. Sorption of Cs to illite was nearly complete at the lowest initial concentration (10^{-5} M) and decreased with increasing concentration. These results are consistent with adsorption of Cs to high affinity frayed edge sites (FES) of illite[8,9] even under the extreme geochemical conditions of STWL. Despite reduced uptake at higher initial concentration, there was a clear long-term kinetic effect that contributed to a slow uptake reaction, particularly in the case of vermiculite (Fig. 2a-c). In the case of montmorillonite systems, continuous Cs uptake was observed during the aging time and more rapid sorption occurred at lowest Cs loading (Fig. 3a-c). In all clays, a substantial mass fraction of Cs was resistant to removal by both Mg^{2+} exchange and AAO extraction, resulting in a large "residual" pool. Furthermore, the amount of Cs sorbed into the residual fraction tends to increase over the course of the experiment. In the montmorillonite case, overall distribution of Cs into exchangeable, AAO extractable and residual pools was relatively consistent despite the large (100-fold) differences in initial Cs concentration.

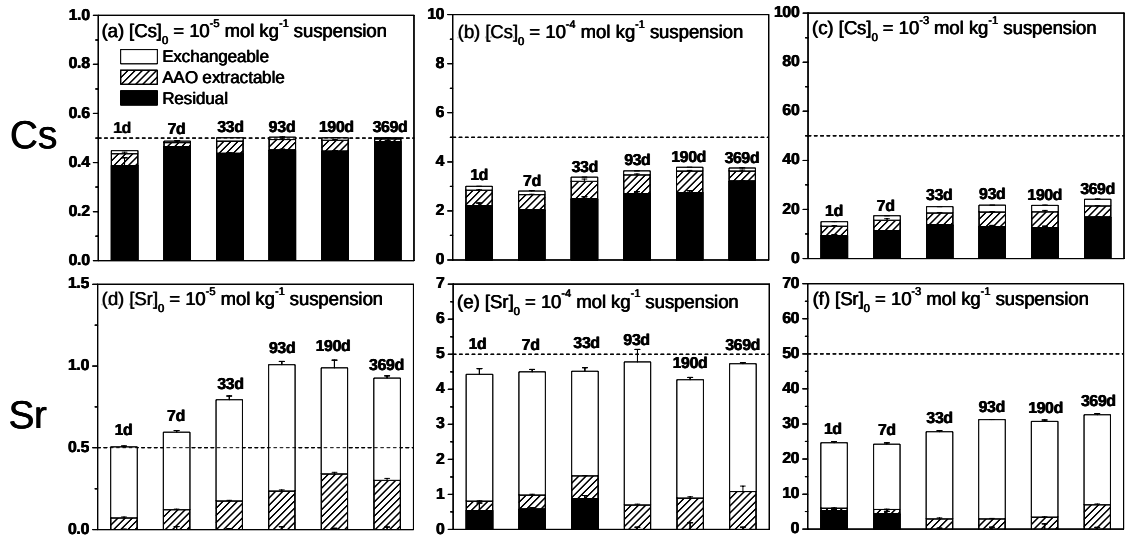

Figure 1. Sorption of Cs and Sr during incongruent dissolution of illite in STWL. Total bar height represents millimoles of Cs and Sr sorbed to the solid phase per kilogram of illite present initially (determined from concentration depletion in the aqueous phase). Complete removal from solution is represented by the horizontal lines at 0.5, 5.0, and 50.0 mmol kg^{-1} for initial contaminant concentrations of 10^{-5}, 10^{-4}, and 10^{-3} M, respectively. The millimoles of Cs and Sr recovered during Mg^{2+} exchange and AAO extraction are indicated, as is the unrecovered or "residual" mass. Error bars show standard deviations of replicate measurements.

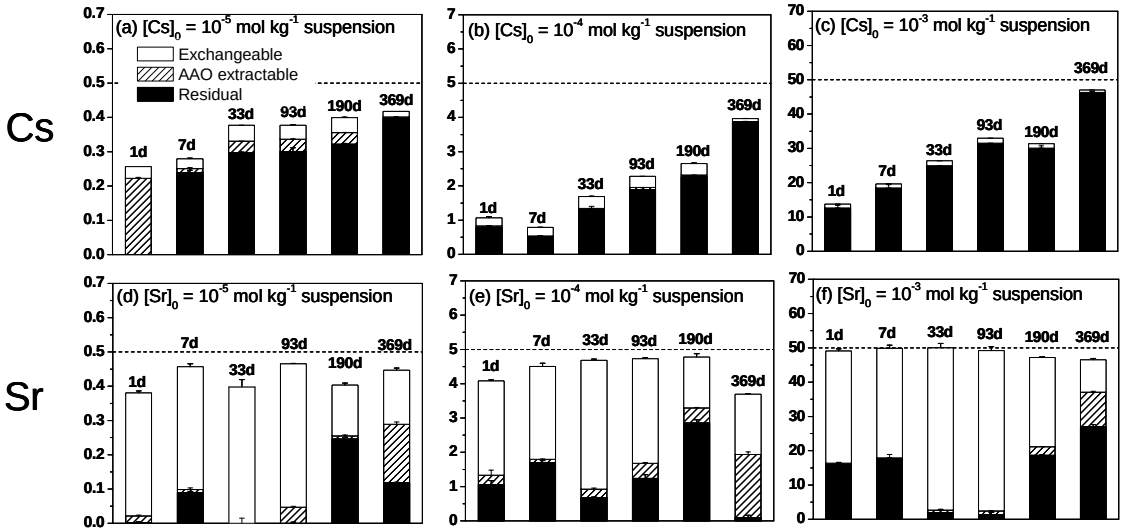

Figure 2. Sorption of Cs and Sr during incongruent dissolution of vermiculite in STWL

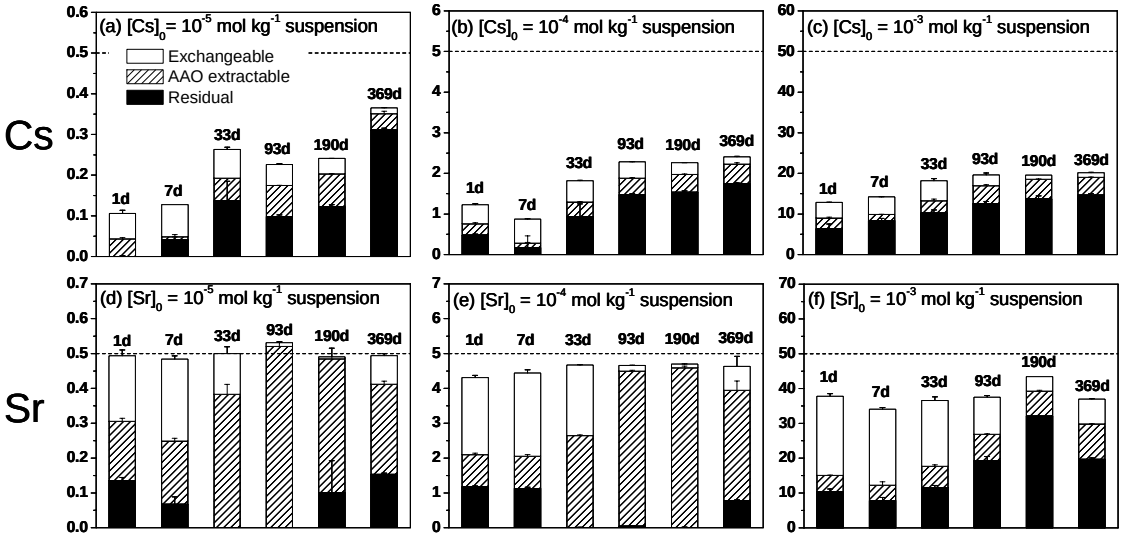

Figure 3. Sorption of Cs and Sr during incongruent dissolution of montmorillonite in STWL.

The sorption of Sr was rapid in all systems and essentially complete removal was observed for the lowest initial Sr concentrations over the reaction period (Fig. 1d, 2d, 3d). At the highest initial concentration, sorptive retention of Sr was greatest for vermiculite, followed by montmorillonite and illite (Fig. 1f, 2f, 3f). Vermiculite was an especially effective sorbent for Sr as uptake was nearly complete for the highest Cs and Sr loading, but sorption decreased slightly with aging time (Fig. 2d-f). Sr sorption to montmorillonite accounted for 99%, 93% and 74% of the initial Sr from solution for initial concentrations of 10^{-5}, 10^{-4} and 10^{-3} M, respectively, after 369 d (Fig. 3d-f). In the illite systems, most sorbed Sr was removed by unbuffered $Mg(NO)_3$ solution irrespective of initial concentrations or reaction stage (Fig. 1d-f). For vermiculite, Mg-exchangeable Sr

was dominant at early times (prior to 93 d for 10^{-5} and 10^{-4} M and prior to 190 d for 10^{-3} M initial Cs and Sr concentrations), but later was incorporated into AAO extractable and residual pools (Fig. 2d-f). This “aging” effect was even more pronounced in the case of montmorillonite, where Mg-exchangeable Sr was converted to increasingly recalcitrant AAO extractable and residual forms over the one-year reaction period (Fig. 3d-f). In general, in montmorillonite, the formation of residual Sr was favored by higher initial Sr concentrations, which suggests co-precipitation of Sr in neo-formed solids. In the case of kaolinite, at earlier times, most sorbed Sr was removed by contacting the solid with unbuffered $Mg(NO_3)_2$ solution and later, Sr was not mobilized by ion exchange; removal required dissolution of poorly crystalline solids in AAO solution. At longer reaction time, Sr was incorporated into nonextractable pools as indicated by an increase in the residual fraction.

The formation of product (“secondary”) phases was detectable with X-ray diffraction (XRD) after 93 d for montmorillonite, 190 d for vermiculite and 369 d for illite. XRD patterns of illite and vermiculite were not as strongly impacted by the one-year reaction although vermiculite had emerging peaks after 190 d, indicating a lower mass fraction of crystalline precipitates. Sodalite peaks emerged at 369 d in illite at all three Cs and Sr loading concentrations. Both major sodalite and cancrinite peaks were identified after 369 d in reacted vermiculite samples. Montmorillonite XRD peaks decreased and broadened with reaction time due to OH^- promoted weathering and new peaks emerged that were attributable to three feldspathoid or zeolite phases: sodium aluminum silicate hydrate (zeolite X), sodium aluminum nitrate silicate (feldspathoid sodalite) and sodium aluminum nitrate silicate hydrate (feldspathoid cancrinite). As reported previously for kaolinite[6] dissolution and secondary mineral formation in montmorillonite systems are clearly controlled by initial Cs and Sr concentrations and aging time, whereas this is not the case for illite and vermiculite. Secondary solids in illite had either elongated or round shapes with an irregular boundary and contained a strong Sr EDS peak with along with O and small amounts of Na, Al, K and Fe. Unlike Sr, there was no isolated high Cs secondary phase in any of the clay systems. EDS spectra of illite particles show that most Cs was detected on edges of clay platelets. In vermiculite, the composition of spherical secondary phases (*ca.* 3.5 µm in diameter) is primarily Si, Al and Na. The major components of spheroidal secondary phases in the montmorillonite system are Si, Al, Na and small amounts of Sr and Cs.

In conclusion, contaminant sequestration behavior exhibited dependence on (i) clay mineral type, (ii) reaction time and (iii) initial contaminant concentration. These effects must be considered in light of potential reactions including adsorption to layer silicate surfaces and incorporation into neo-formed, solid-phase weathering products. Because of Cs and Sr-containing secondary phases in reacted clay, the long-term stability of secondary phases, which is clearly central to their environmental impact, needs to be evaluated.

ACKNOWLEDGEMENTS
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