Clay mineral weathering and contaminant dynamics in a caustic aqueous system

II. Mineral transformation and microscale partitioning

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Abstract—Microscopic and spectroscopic studies were conducted to assess mineral transformation processes in aqueous suspensions of illite (II), vermiculite (Vm) and montmorillonite (Mt) that were subjected to weathering in a simulated high-level radioactive tank waste leachate (0.05 m AlT, 2 m Na+, 1 m NO3, pH ~14, Cs+ and Sr2+ present as co-contaminants). Time series (0 to 369 d) experiments were conducted at 298 K, with initial [Cs]0 and [Sr]0 concentrations from 10-7 to 10-3 mol kg-1. Incongruent clay dissolution resulted in an accumulation of secondary aluminosilicate precipitates identified as nitrate-sodalite, nitrate-cancrinite and zeolite X, by molecular spectroscopy and electron microscopy (XRD, FTIR, SEM-EDS and TEM-EDS). Contaminant fate was dependent on competing uptake to parent clays and weathering products. TEM-EDS results indicated that high II affinity for Cs was due to adsorption at frayed edge sites. The II system also comprised Sr-rich aluminous precipitates after 369 d reaction time. In Mt systems, Cs and Sr were co-precipitated into increasingly recalcitrant spheroidal precipitates over the course of the experiment, whereas contaminant association with montmorillonite platelets was less prevalent. In contrast, Cs and Sr were found in association with weathered Vm particles despite the formation of spheroidal aluminosilicate precipitates that were comparable to those formed from Mt dissolution. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

~373,400 m³ of high level radioactive waste have been stored in underground steel tanks at Department of Energy (DOE) sites across the U.S. including Hanford, WA; Savannah River, SC; Idaho Falls, ID; West Valley, NY and Oak Ridge, TN (DOE, 1995; Ahearne, 1997). Most of this waste (63%) is stored at the Hanford facility in 177 tanks ranging in size from 210 to 4100 m³ (Ahearne, 1997). Of these tanks, 67 have leaked, causing the release of over 3800 m³ of highly radioactive liquid waste containing 137Cs and 90Sr into the underlying sediment (Zachara et al., 2002). The leaking tank waste is characterized by high pH (> 13), high aluminophase concentrations, and high ionic strength (dominantly NaNO3) (Serne et al., 2001). The sediments at the Hanford site comprise micaceous weathering products illite, vermiculite and montmorillonite (Serne et al., 2001) that are expected to contribute to Cs and Sr attenuation in the vadose zone. Under circumneutral conditions, these clay minerals exhibit variable affinities for Sr, and particularly Cs, depending on the density and location of charge resulting from isomorphic substitution (Sawahney, 1972; Onodera et al., 1998; Sutton and Sposito, 2001; Zachara et al., 2002). However, they are also susceptible to high rates of dissolution at the caustic pH values encountered in tank waste leachate (Nagy, 1995; Chorover et al., 2003).

In a companion paper, we reported on the time-dependent coupling between Cs and Sr uptake and clay mineral (illite, vermiculite and montmorillonite) dissolution in a tank waste simulant (Choi et al., 2005). Dissolution rates were dependent on clay mineral type and co-contaminant concentrations, and reprecipitation of secondary solid phase products was evident in all systems. The objective of the present study was to employ microscopic and spectroscopic techniques to identify the nature of mineral transformations responsible for the element solubility patterns observed by Choi et al. (2005), and to elucidate the solid-phase fate of Cs and Sr in the weathering clay systems.

2. MATERIALS AND METHODS

Montmorillonite (SWy-2) from Crook County, WY and illite (I Mt-1) from Silver Hill, MT (both dioctahedral) were obtained from the Source Clays Repository of the Clay Minerals Society. trioctahedral vermiculite from Phalaborwa in Transvall of South Africa was obtained from Ward’s Scientific Inc., NY. Conventional mineralogical characterization (K and Mg saturation, ethylene glycol and glycerol solvation, and heat treatments) of this vermiculite sample by XRD (following cleaning) indicated that it contained no detectable illite interstratification or hydroxy-interlayering. All clays were size fractionated, cleaned, saturated with NaCl, and maintained as clay suspensions before experiments. Clay samples were then reacted in a synthetic tank waste leachate (STWL) solution. The STWL was composed of ultrapure (MilliQ) water with 2.0 mol kg-1 Na+, 1 mol kg-1 NO3, 1 mol kg-1 OH- and 0.05 mol kg-1 AlT to simulate the chemistry of Hanford tank waste leachate (Serne et al., 1998). The synthetic tank waste leachate (STWL) was spiked to give three initial aqueous phase Cs+ and Sr2+ concentrations, where each contaminant was added at a solution concentration of 10-8, 10-4 or 10-3 mol kg-1, and both cations were present at equal concentration in all systems to compare co-contaminant fate. Batch experiments were conducted in sealed 60 mL polypropylene copolymer (PPC0) bottles. All suspension clay concentrations were 20.0 g kg-1 (0.50 g dry mass in 25.0 g of STWL) to give similar total moles of Si in each batch reactor.

The batch reactors were placed on an end-over-end shaker at 2 rpm and two sets of duplicates were sampled for solid phase analysis after 1, 7, 33, 93, 190 and 369 d. Suspensions were transferred quantitatively to PPC0 bottles and centrifuged at 28,700 g for 20 min. The centrifuged pellets were resuspended in 95% ethanol (adjusted to pH 10 with 1 M NaOH) and centrifuged to remove entrained salt solution. Two more
ethanol washes were conducted without pH adjustment. Two samples were removed, dispersed in 15 mL of MilliQ water, frozen immediately at −80°C, and then freeze dried before analysis. Duplicate samples were resuspended in 33.0 g of 0.1 m Mg(NO₃)₂, shaken for 1 h and then centrifuged at 28,700 g for 20 min to extract weakly-bound Cs and Sr. Pellets were then washed three times with 0.2 M ethanol before being resuspended in 0.2 m acidic ammonium oxalate solution (AAO) (4 h at pH 3 on a reciprocal shaker in the dark) to extract “poorly-crystalline” precipitates (Jackson et al., 1986). The samples were centrifuged at 28,700 g and the supernatant solution was decanted. The samples were then washed with 0.1 and then 0.01 m NaCl to remove residual AAO solution, before freeze drying. Further details on reaction conditions and solution phase chemistry are discussed in Choi et al. (2005).

Analysis of the reacted clay samples before and after AAO extraction involved a multi-faceted approach. X-ray diffraction (XRD) analyses were conducted on randomly-oriented powder samples mounted on zero background quartz slides using a Scintag diffractometer with CuKα radiation, and a PAD X-418, 2θ-θ goniometer with a Ge solid state detector at 35kV and 30mA. The divergent and receiving slits were 2.0 and 0.3 mm, respectively. Samples were scanned at 2° 2 0 min−1 from 3° to 70° 2 0. For precise interpretation of samples reacted for 369 d, we used a Philips X’pert MPD diffractometer equipped with a spinning stage and X’Celerator multiple strip detector with Ni-filtered CuKα radiation at 50 kV and 40 mA. Data were collected from 30° to 80° 2 0 in continuous scan mode with a step size of 0.017°. The divergent slit was 0.0625°. Samples were back-filled into 15 x 5 mm circular spinning holders. Reacted samples were also examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), both equipped with energy dispersive X-ray spectroscopy (EDS) capability. SEM analyses were conducted on an FEI-Philips XL-20 and an Hitachi S-2460N SEM at 25 kV. Samples were prepared for TEM by grinding gently with an agate mortar and pestle, dispersing in acetone, and then transferring the suspended material onto a carbon lacey Cu grid for analysis using a Hitachi H8100 LaB₆, unit operating at 200 kV. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained on freeze-dried samples over a wavenumber range from 4000–400 cm⁻¹ at a linear resolution of 4 cm⁻¹ using a Nicolet Magna 560 FTIR spectrometer. DRIFT samples were prepared by gently grinding 14 mg of sample, and then folding the mass in with 400 mg of IR grade KBr powder.

Solid-state 27Al nuclear magnetic resonance (NMR) with magic angle spinning (MAS) analyses were performed on the reacted Mt samples using a Varian 500 MHz NMR spectrometer operating at a magnetic field strength of 11.74 T and a 27Al resonance frequency of 130.188 MHz. The X- channel of a 5 mm Chemagnetics HX double resonance MAS probe was used. Single-pulse 27Al spectra were measured using short radio frequency pulses of 0.60 μs (equivalent to a 10° tip angle for the central transition), spinning rates of 10.0–10.5 kHz, and a recycle delay of 1.0 s. Free-induction decays of 4096 data points were processed with an exponential windowing function corresponding to a line broadening of 100 Hz. The 27Al chemical shifts (in ppm) are referenced to an external sample of 1 M Al(H₂O)₆³⁺. The use of short radio frequency pulses ensures accurate quantification of the resonances from four- and six-coordinate aluminium, which can have substantially different quadrupolar coupling interactions (Man et al., 1988).

### 3. RESULTS

#### 3.1. Scanning Electron Microscopy

In accordance with the Si and Al dissolution results (Choi et al., 2005), secondary phases were not detected in the illite systems by SEM before 190 d, regardless of Cs and Sr concentration. However, illite particles were found to decrease in size relative to unreacted samples (Fig. 1a) with increasing reaction time. At 190 d, precipitates with a ‘bundle of yarn’ (BY) shape were clearly evident, and subtle morphologic differences were observed between the treatments (Fig. 1b-c). The spheroidal phases were composed of intergrown disks.

Unreacted vermiculite has clean sheet-like surfaces devoid of secondary phases (Fig. 1d). Irrespective of Cs and Sr loading, BY-shaped secondary phases, ~4 μm in size with sharp edges, were readily identified at 190 d (Fig. 1e). After 369 d, the precipitates assumed a more irregular shape than was observed at 190 d (Fig. 1f) and edges were not as sharp. SEM results confirm that AAO treatment effectively removed all secondary precipitates from both illite and vermiculite samples over all reaction times (not shown).

Unreacted montmorillonite comprises large flakes (Fig. 2a). Circular (ca. 1 μm diameter) (Fig. 2b) and lath-shaped (ca. 1 μm long) (Fig. 2c) particles precipitated on montmorillonite surfaces at 10−3 m Cs and Sr after 1 and 7 d, respectively. Euhehedral-shaped secondary solids formed in 10−3 m Cs/Sr after 33 d (Fig. 2d). After 190 d, montmorillonite surfaces contain cubic crystals intergrown with spheroidal bundles of platy-shaped precipitates at 10−3 m Cs and Sr (Fig. 3a). 190 d, illite particles were found to decrease in size, precipitate morphology was similar to those observed at 190 d, but surfaces were more irregular in shape (Fig. 3d). After 369 d at the highest Cs/Sr concentration, precipitate morphology was dominantly as shown in Figure 3e. However, after treatment with AAO, nitrate cancrinite is revealed with its elongated c-axis within the spheroidal precipitates (Fig. 3f).

Fig. 4 shows back scattered electron images with EDS spectra from X-ray analysis conducted on samples without preparative coating. Solid arrows on each image show the area for which EDS spectra were obtained. In reacted illite, we detected particles (ca. 1.8 μm) with Sr as the major constituent and smaller amounts of C, Al, O, K and trace amount of Fe (Fig. 4a). The latter elements reflect the illite component itself. Spheroidal BY-shaped secondary particles (ca. 3 μm diameter) show Si, Al, Na, C, O, Fe and K with Sr as a minor component (Fig. 4b). A Si:Al peak area ratio close to unity was commonly observed for secondary phases, consistent with similar AAO Si and Al values for illite and vermiculite (Choi et al., 2005). In the case of vermiculite, EDS spectra of reacted vermiculite particles show Si, Al, Mg, Na and Fe as major components and Ti, K and Cs as minor components (Fig. 4c). Secondary solids observed in montmorillonite (ca. 4 μm diameter) comprised Si, Al, Na and O as major components, and Fe and Sr as minor components (Fig. 4d). As in illite, the Si:Al peak ratio of spheroidal phases was ~1:1.

#### 3.2. X-ray Diffraction

Unreacted (Na-saturated) II, Vm and Mt showed 10.20, 12.20 and 12.69 Å basal spacings, which is close to published values of Na-saturated forms of these clay minerals (Brindley, 1980). However, after 369 d, basal spacings were 9.96 (II), 12.24 to 12.26 (Vm), and 12.34 to 12.37 Å (Mt), with the higher values at higher contaminant loading (Fig. 5). Basal spacings of the clays showed clear decreases in intensity and broadening with reaction time. This effect is most evident for Mt (Fig. 5c). The formation of crystalline reaction products was detectable after 93 d for Mt, 190 d for Vm, and 369 d for II.
Sodalite peaks (identified by the 6.34 Å reflection since the major sodalite peak at 3.66 Å was obscured by principal illite reflections) were detected in II at all three Cs and Sr concentrations after 369 d (Fig. 5a). Overall, there was no effect of Cs and Sr loading on peak intensities in II, but an unidentified peak near 5.69 Å was observed in the highest Cs and Sr loading. In Vm systems, small cancrinite and sodalite peaks were detected and, as in II, emergent relative peak intensities were independent of initial Cs and Sr concentration (Fig. 5b). More distinct secondary peaks were observed in Mt systems (Fig. 5c) and these are attributable to three feldspathoid or zeolite phases: sodium aluminum silicate hydrate (zeolite X; \(Na_{17.52}Al_{24}Si_{24}O_{96}H_{6.48}\), \(d\)-spacing 14.35 Å) (International Center for Diffraction Data, Newtown Square, PA, 2000; Card No. 72-2422), sodium aluminum nitrate silicate (feldspathoid cancrinite; \(Na_8(Al_6Si_6O_{24})(NO_3)_2\cdot 4H_2O\), \(d\)-spacing 3.24 Å) (International Center for Diffraction Data, Newtown Square, PA, 2000; Card No. 38-0513). The \(d\)-spacing of zeolite X in our system is slightly larger than in ICDD, but all peaks are closely matched.

The full time series of XRD results are shown for Mt in Figure 6. Sodalite produces a strong XRD peak that emerges earlier than that of cancrinite, although cancrinite is more easily observed by SEM because of its larger particle size. Also, it is observed that decrease in basal spacing (\(d\)-001) intensities correlate negatively with initial Cs and Sr concentration. For II and Vm, there was no significant decrease in \(d\)-001 intensity during the reaction times (data not shown). Results match with Si chemistry data on our companion papers (Choi et al., 2005). Released amount of Si content was greatest in the order of Mt, Vm and II.

Fig. 1. SEM images of illite (Il) and vermiculite (Vm) samples: (a) unreacted illite; (b) spheroidal ‘ball of yarn’-shaped secondary solids in Il (10^{-3} mol kg^{-1} Cs/Sr, 190 d); (c) secondary solids formed in Il (10^{-3} mol kg^{-1} Cs/Sr, 190 d); (d) unreacted platy vermiculite; (e) bundles of spheroidal secondary solids on vermiculite surfaces (10^{-3} mol kg^{-1} Cs/Sr, 190 d); and (f) spheroidal secondary solids in reacted vermiculite (10^{-3} mol kg^{-1} Cs/Sr, 369 d).
The time-dependent change in XRD peak intensity ratios of sodalite (3.65 Å) and cancrinite (3.23 Å) to montmorillonite (d-001) are plotted in Figure 7. Beginning at 93 d, fastest growth of both product peaks occurs at the lowest Cs and Sr concentration; there is a lag in peak emergence and a slower rate of growth at higher Cs/Sr concentration. The intensity ratio for sodalite exceeds that for cancrinite over the full reaction time, but the rate of cancrinite peak growth exceeds that for sodalite between 193 and 369 d (Fig. 7). AAO treatment of the 369 d Il and Vm samples resulted in complete elimination of product peaks, whereas this was not the case for Mt. In Mt systems, cancrinite, sodalite and zeolite X were detectable by XRD after AAO extraction at the lowest Cs and Sr loading, but only sodalite was detected after extraction at the highest loading.

3.3. Diffuse Reflectance Fourier Transform Infrared (DRIFT) Spectroscopy

Emerging absorption bands at 1425 cm\(^{-1}\) and 1380 cm\(^{-1}\) were observed in all reacted systems, but their intensity varied with treatment. For Il, these bands were small and of similar intensity, whereas for Vm they were larger, and absorbance at 1425 cm\(^{-1}\) was slightly greater than at 1380 cm\(^{-1}\) (not shown). The bands were most developed in Mt, where their relative intensities were dependent on initial Cs and Sr concentrations; the absorption intensity ratio 1380 to 1425 cm\(^{-1}\) decreased from 10\(^{-5}\) to 10\(^{-3}\) m Cs/Sr (Fig. 8).

These IR absorption bands are indicative of enclathrated guest anionic species in the zeolites (Buhl, 1993a; Buhl and Löns, 1996; Hackbarth et al., 1999; Buhl et al., 2000). The ca. 1380 cm\(^{-1}\) band is assigned to nitrate intercalation within the sodalite cages (Buhl, 1991a, 1991b; Buhl and Löns, 1996; Fechtelkord et al., 1997). A band at 1450 cm\(^{-1}\) has been attributed to absorbance resulting from the CO\(_3\) stretching vibration of carbonate-containing sodalites and cancrinites (Buhl, 1991b; 1993a, 1993b; Hermeler et al., 1991; Buhl et al., 1997; Hackbarth et al., 1999), but inorganic C concentrations in our equilibrium solutions were very low in our systems (< 2 mM). Therefore, following Buhl and coworkers, we attribute the 1425 cm\(^{-1}\) band in Figure 8 to structural distortion in the nitrate cancrinite structure, which results in splitting of the NO\(_3\) vibration between 1380 and 1425 cm\(^{-1}\) (Buhl and Löns, 1996; Hackbarth et al., 2000; Chorover et al., 2003). Thus, the 1380 cm\(^{-1}\) band contains contributions from both nitrate sodalite and nitrate cancrinite, whereas the 1425 cm\(^{-1}\) band results dominantly from nitrate cancrinite.

Quantification of the 1425 and 1380 cm\(^{-1}\) absorbance intensities indicate that nitrate-containing secondary solids increase in prevalence in the order Il < Vm < Mt, consistent with the XRD results. However, the DRIFT data are more sensitive than XRD because they reveal incipient precipitation of secondary phases at earlier times, which is also consistent with SEM observations (Figs. 1–3). The rate of nitrate peak growth was fastest in the case of Mt, followed by Vm and then Il. In Mt, absorption bands at ca. 1380 cm\(^{-1}\) indicative of nitrate-containing sodalite and cancrinite, be-
gan to emerge at $10^{-5}$ m and $10^{-4}$ m Cs and Sr at 93 d (Fig. 8). At long reaction times (> 33 d), an inverse relation was observed between nitrate (1380 cm$^{-1}$) peak intensity and the initial concentration of Cs and Sr in Mt systems (Fig. 9).

Secondary phase formation is also indicated by changes in water IR absorbances. The broad O-H stretch at 3100–3600 cm$^{-1}$ and the bending mode near 1650 cm$^{-1}$ can be assigned to water molecules (Buhl, 1991a, 1991b; Hermeler et al., 1991; Veit et al., 1991; Buhl et al., 2000). The intensities of these water IR bands increased with reaction time for Mt (Fig. 8), but not apparently in Il and Vm. The O-H stretch in Mt systems showed higher absorbance at lower initial Cs and Sr concentrations (Fig. 8). Both structural (as in cancrinite) and adsorbed (as in poorly crystallized precipitates) water are likely contributing to these peaks.

AAO treatment of Il and Vm after 369 d removed the 1380 cm$^{-1}$ band, but a small band at 1425 cm$^{-1}$ remained. In Mt, both bands remain after AAO treatment of 369 d reacted samples, but the 1425 cm$^{-1}$ absorbance is increased in intensity relative to the 1380 cm$^{-1}$ peak (Fig. 10). These results indicate that the nitrate-containing solids exhibit increasing resistance to dissolution (i.e., increasing crystallinity) with reaction time.

In addition to the nitrate and water stretching vibrations, asymmetric and symmetric T-O-T (T = Si, Al) bending modes of the zeolite framework reveal characteristic—albeit weaker —resonance lines in the midinfrared (Flanigen et al., 1971; Buhl, 1991b; Fechtelkord et al., 2001; Gesing and Buhl, 1998). On this basis, the “fingerprint” of sodalite can be readily distinguished from that of cancrinite (1000–400
Characteristic fingerprint peaks for sodalite in Mt are observed at 661, 703 and 730 cm\(^{-1}\) after 93 d (Fig. 8c). At low and intermediate Cs and Sr loading, cancrinite framework absorbances (1030, 1008, 985 cm\(^{-1}\)) and T-O-T vibrations (689, 624 and 576 cm\(^{-1}\)) (Zheng et al., 1997; Buhl et al., 2000) emerge after 93 d, though not as strongly as sodalite. Time-dependent growth of IR absorbances at 731 and 624 cm\(^{-1}\) for sodalite and cancrinite, respectively, indicate more rapid accumulation of both phases with decreasing co-contaminant concentration (Fig. 11).

### 3.4. Solid State \(^{27}\)Al Nuclear Magnetic Resonance

Solid-state \(^{27}\)Al NMR spectra were collected on reacted Mt over the full range of Cs and Sr concentrations and reaction times (Fig. 12a). Unreacted Mt shows two broad resonances near at 4.5 ppm and 61 ppm from six- and four-coordinate aluminum, respectively, the latter reflecting a detectable but small amount of Al substitution in the tetrahedral sheet. With increasing reaction time, an asymmetrical resonance composed of multiple Al environments develops in the 40–70 ppm range.
indicating the formation of secondary phases containing four-coordinate aluminum. The proportions of solid-phase Al in secondary phases were calculated as a function of reaction time and co-contaminant concentration by the integrating peak area ratio \( \frac{[\text{Al}^4]}{[\text{Al}^4 + \text{Al}^6]} \) from \(^{27}\text{Al}\) NMR data (Fig. 12b). Upon integration of four- and six-coordinate aluminum peak

Fig. 5. X-ray diffraction patterns of randomly-oriented, unreacted (a) illite, (b) vermiculite and (c) montmorillonite before (unreacted) and after reaction (369 d) at initial solution Cs and Sr concentrations of \(10^{-5}, 10^{-4}\) and \(10^{-3}\) mol kg\(^{-1}\). (▽ sodalite, ● cancrinite, ▼ zeolite X and ○ unnamed secondary phase).

Fig. 6. X-ray diffraction patterns of randomly-oriented Mt collected as a function of reaction time up to 369 d at initial solution Cs and Sr concentrations of \(10^{-5}, 10^{-4}\) and \(10^{-3}\) mol kg\(^{-1}\). (▽ sodalite, ● cancrinite, and ▼ zeolite X).
intensities, we confirm that initial Cs and Sr concentrations affect the rate at which secondary phases form. Evidently, higher concentrations of Cs and Sr inhibit precipitation, consistent with our semiquantitative analysis deriving from XRD and DRIFT.

3.5. Transmission Electron Microscopy

TEM with EDS and electron diffraction (ED) was employed to locate Cs and Sr in the weathered clay systems. Strontium enriched particles with irregular boundaries were observed in II systems and were found to comprise also Si, O, C and small amounts of Na, Al, K and Fe (Fig. 13a, EDS spot size is 100 nm). After correcting for the ED pattern of superimposed illite crystals (electron diffraction spot size is 1 μm), the following d-spacings were determined for the Sr-rich phase: 4.64, 4.43, 4.13, 3.54, 3.10, 2.92, 2.49, 2.30, 2.06, 1.65, 1.25 and 0.98 Å. This solid is more likely Sr-aluminosilicate than SrCO₃ because the d-spacings do not match with the latter and the EDS spectrum shows a significant Si peak, and a smaller Al peak. An Fe-rich, faceted crystal of ca. 2 μm in size was also observed in reacted II systems (Fig. 13b). The Fe-rich particles show a significant Sr peak, whereas the Si, Al and K may derive predominantly from the illite matrix. ED patterns of the faceted iron particle were not diagnostic, but revealed d-spacing values, after matrix correction, of 2.32, 3.59 and 4.7 Å. In II systems, spheroidal secondary phases ca. 5 μm in diameter with apparent Si:Al mass ratio close to unity, and high Na concentration were evident (Fig. 13c). In addition to O, C and Fe, the EDS spectrum shows Sr incorporation in this phase. The ED patterns of these particles reveal d-spacing values of 3.24, 2.83 and 2.16 Å. The first two values match with sodalite and the latter with cancrinite, indicating that the round-shaped secondary phases are an intergrown mixture of these two phases. There were no isolated Cs-enriched secondary solids detected in any of the clay systems, although Cs sorption to the layer silicate particles themselves was observed. EDS spectra of illite platelets show Cs associated

![Fig. 7. XRD peak intensities of (a) sodalite and (b) cancrinite relative to the basal spacing of montmorillonite as a function of reaction time and initial solution Cs and Sr concentration.](image)

![Fig. 8. Time-series of DRIFT spectra for Mt over the 1 year reaction time at three initial Cs and Sr solution concentrations.](image)
with edges, rather than the collapsed interlayers of clay particles (Fig. 13d.). In contrast, Sr was not detected in association with illite particles.

In Vm, the elemental composition of spherical secondary phases (ca. 3.5 μm in diameter) is dominantly Si, Al and Na (Fig. 14a). Their morphology is composed of hexagonal plates or disks on edge combined with needle-shaped crystals. The Si:Al ratio is close to unity, and all of the probed secondary particles contain Na and sometimes small amounts of Fe. The ED patterns of secondary phases in Vm have d-spacings of 6.36, 3.66 and 2.11 Å, nearly identical to those observed in Il, and consistent with Na-containing sodalite and cancrinite. Secondary solids containing high Cs and/or Sr concentrations were not detected in Vm. Cesium and Sr were detected in the vermiculite clay particles themselves (Fig. 14b), which is consistent with the high sorbed fractions of these elements at 369 d in Vm (Choi et al., 2005). The spherical secondary particles (intergrown cancrinite and sodalite) were most prevalent in Mt systems (Fig. 15a). However, unlike the case for Il and Vm, the ED patterns of these particles rapidly disappear under electron beam exposure, suggesting that these zeolites are susceptible to radiation damage (Gu et al., 2000; Wang et al., 2000). EDS data indicate that they comprise dominantly Si, Al (with Si:Al ~ 1) and Na, in addition to smaller amounts of Sr and Cs (Fig. 15a). EDS peak intensities of Na, Sr and Cs were variable among these particles, and some showed no detectable contaminant retention. As in the case of Vm, ED results show that the particles are not a single phase, but rather that they are compositionally heterogeneous. On individual particles, d-space values of 2.16 Å were indicative of cancrinite, those at 3.24, 2.83 and 2.55 Å are consistent with sodalite, and those at 5.7 and 3.79 Å derive from zeolite X. As in Il, the Mt system produced an Fe-rich solid phase comprising Sr that had faceted isometric morphology and faint ED patterns (Fig. 15b). Only small amounts of Sr were associated with montmorillonite particles themselves (not shown). Also, despite a similar amount of Cs uptake in Il and Mt, no Cs was found in montmorillonite particles.

4. DISCUSSION

Chemical reaction of 2:1 layer-type clays with a caustic high level radioactive waste simulant (STWL) affects the fate of contaminant radionuclides through concurrent adsorption and dissolution-precipitation reactions. Whereas mineral transformation is normally slow relative to adsorption-desorption, the former becomes relevant at the time-scale of the current experiments because reaction of STWL with clays promotes rapid Si dissolution. Our prior work indicated that initial Cs and Sr concentrations affect the rate of release of Si from layer silicate clays and its accumulation in AAO extractable products (Chorover et al., 2003; Choi et al., 2005). The present study indicates that these AAO extractable phases include sodalite, cancrinite and zeolite X (the latter only in Mt systems), and their formation may lead to sequestration of Cs and/or Sr, depending on the competing effect of clay mineral affinity for the radionuclides.

4.1. Effect of Parent Clay Mineral Type

The type of clay impacted the fate of Cs and Sr in two ways, (i) by exhibiting a range in affinity for adsorptive uptake of the contaminants to the clays themselves and (ii) by virtue of their variation in Si dissolution rates. Timing of secondary phase formation as observed by SEM, TEM and spectroscopy corresponds with the drop in aqueous Si concentration reported in Choi et al. (2005). The spheroidal particles observed in all clay systems (Fig. 1, 3, 4, 13c, 14a, 15) are composed of intergrown cancrinite and sodalite (and zeolite X in Mt) and incorporate variable amounts of Cs or Sr. Whereas Na is the charge balancing cation in the chemical formulae presented, substitution of Cs and Sr2 for Na is certainly possible (Norby et al., 1991; Liu and Grey, 2002). In addition, we also observed a Sr-rich silicate phase in illite and Sr-containing Fe solids in Il and Mt.

Our results suggest that the quantity of Cs and Sr incorporated into the feldspathoid and zeolite weathering products depends on both the accumulation rate of these neoformed solids, and also on the availability of Cs and Sr in the aqueous phase. If the contaminant ions are removed from solution by sorption to the parent clay surface (particularly to high affinity
sites), then their sequestration into solid phase weathering products is diminished. Cesium is effectively sorbed to frayed edge sites of illite (Fig. 13d) such that it is not found in association with zeolite particles formed from illite dissolution, whereas Sr containing secondary solids were observed in those systems (Fig. 13a–c). This result is consistent with high illite selectivity for Cs relative to Sr (Jeong et al., 1996; Dyer et al., 2000; Zachara et al., 2002) and the limited density of accessible charged sites in illite \((/H11021150 ppm_{c kg}/H110021)\) for sorption of the hydrated Sr ion. Both Sr and Cs showed near complete sorption to vermiculite platelets after 1 y reaction time as indicated by wet chemistry data (Fig. 4 in Choi et al., 2005) and TEM-EDS results (Fig. 14b), whereas the neoformed sodalite-cancrinite particles showed no detectable Cs or Sr incorporation (e.g., Fig. 14). The decreased basal spacing of Il is likely induced by Cs uptake and interlayer collapse, whereas the increased basal spacing of Vm and Mt reflect uptake of both Cs and hydrated Sr ions (Fig. 5). The lack of Sr sorption to illite particles themselves is presumably because the non-expandable clay can not accommodate the large size of the hydrated Sr ion.

Mass normalized Si release rates increased in the order illite < vermiculite < montmorillonite (Choi et al., 2005). The appearance of neoformed solids earliest in the Mt systems can be attributed to the more rapid achievement of supersaturation resulting from the high Si dissolution rate of montmorillonite, and precipitation of sodalite, zeolite X and cancrinite (Fig. 6) from crystallization of soluble silica and aluminate with \(NO_3^-\), \(OH^-\) and \(H_2O\). Sodalite and cancrinite XRD peaks were also observed in Vm systems, while only sodalite peaks were observed in Il (Fig. 6). However, since SEM images of reacted Il provided evidence for formation of crystals with cancrinite morphology similar to that observed in Vm and Mt (Fig. 1b-c), we conclude that the abundance of these reaction products in Il was insufficient to provide sufficient XRD signal.

### 4.2. Formation and Composition of Zeolite Precipitates

Co-existence of cancrinite and sodalite has been reported under a range of alkaline, high ionic strength conditions where both Al and Si are prevalent (Gerson and Zheng, 1997; Fechtelkord et al. 2001). Cancrinite has a hexagonal crystal system and space group \(P6_3\) with AB-AB layer-type packing (Grundy and Hassan, 1982; Hassan and Grundy, 1991; Meier...
Fig. 13. TEM images with electron diffraction patterns and EDS spectra of illite systems (10⁻³ m Cs and Sr, 369 d): (a) Sr-enriched aluminosilicate phase, (b) Fe solid with high Sr, (c) spheroidal secondary phase with Si/Al ratio of ca. 1.0 and (d) reacted illite particle with adsorbed Cs.
and Olson, 1992), which gives rise to large continuous channels parallel to the $c_3$ axis and chains of smaller undecahedral cages along the threefold axes (Hassan and Grundy, 1991). Sodalite, which has a cubic crystal structure (space group P $[mac]43n$), lacks channels due to its ABC layer packing, but has a network of large cages (Zheng et al., 1997; Barnes et al., 1999). Zeolite X was observed in our Mt systems, but not in II or Vm. This zeolite belongs to the isometric crystal system and space group Fd 3 with a 25.01 Å lattice parameter.

Barnes et al. (1999) reported initial precipitation of sodalite with subsequent transformation to cancrinite in spent Bayer liquor. Our experiments also showed the initial formation of sodalite was followed by cancrinite (Fig. 6), but continuing clay mineral dissolution hinders our ability to discern whether sodalite is a necessary precursor for cancrinite formation in this case. Even in Mt systems where kinetics of mineral transformation were most rapid, both sodalite and cancrinite were still present after 369 d reaction time (Fig. 6) and peak intensities for both solids were increasing (Fig. 7). It seems plausible that sodalite consumed during transformation to cancrinite was being continually replenished by clay mineral dissolution throughout the duration of the experiment. This is consistent with the higher aqueous solubility of sodalite (Barnes et al., 1999) and the tendency for Ostwald ripening to the less soluble phase (Lasaga, 1998).

The morphologies of secondary solids observed in these clay systems, including the BY-shaped particles, have been reported by others studying comparable, but not identical, systems in the absence of radionuclides. Zhao et al. (2004) reported cancrinite and sodalite precipitation from reaction of kaolinite (KGa-1, KGa-2) with a tank waste simulant at 323 and 353 K for up to 2 months. Nitrate-cancrinite precipitation was observed to result from reaction of a caustic waste simulant with quartz, a mixed sample of quartz and biotite, and Hanford sediment (Bickmore et al., 2001; Um et al., 2005). The use of higher temperature (323 and 353 K) resulted in greater solid phase crystallinity than observed in the present work at 298 K (Deng et al., 2004; Zhao et al., 2004; Um et al., 2005).

Zeolites formed in these experiments from clay mineral weathering are known to exhibit a high selectivity for specific radionuclides because their structure results in uniform, molecular-sized pores, high internal surface area, high structural charge (from tetrahedral Al occupancy) and reversible hydration properties (Atkins et al., 1995; Sinha et al., 1995; Valcke et al., 1997; Dyer and Zubair, 1998; Adabbo et al., 1999; Qian et al., 2001). Indeed, selective cation exchange is the basis for using zeolites to remove radionuclides such as Cs, Sr, lanthanides and actinides from high-level waste, and their use has been explored as a potential remediation alternative for the Hanford site (Marinin and Brown, 2000). Zeolite formation is
strongly influenced by pH, temperature, Si/Al ratio and aqueous cation composition (Barrer, 1982; Belhekar et al., 1995; Dyer and Zubair, 1998), and sorbent properties are likely to follow suit. One of the critical factors controlling Cs and Sr uptake by zeolites is their structural charge, which correlates negatively with the Si/Al-ratio of their aluminosilicate framework. The data presented here indicate the formation of zeolites with low molar Si:Al ratios $\sim 1$, and therefore high structural charge, because of the high aluminate concentrations in solution.

Neoformed precipitates in our Mt systems show weak resistance to radiation damage under electron beam exposure and this is relevant to their role in sequestering contaminants in the field. Zeolite properties, such as Cs or Sr retention, may be altered as a result of radiation-induced crystalline-to-amorphous transitions at temperatures in the range of 400 to 900 °C (Kosanovic et al., 1996, 1998; Colantuono et al., 1997; Alberti et al., 2001; Joshi et al., 2002). Thermal treatment and dehydration cause the rearrangement of extra-framework cations and residual water molecules (Gu et al., 2000; Hunger et al., 2000). For example, Gu et al. (2000) found that radiation-induced crystalline-to-amorphous transformation of Cs-exchanged zeolite NaY reduced ion exchange capacity over time, but it also enhanced the retention of Cs against desorption by blocking structural channels. Further research is needed to quantify the potential for radionuclide immobilization in the context of high heat and radioactivity common in the impacted environments.

5. CONCLUSIONS

Interacting effects of clay mineral (i) transformation rate and (ii) adsorption affinity combine to influence the localized siting of sorptive cesium and strontium ions in clay systems subjected to weathering in a STWL representative of that released into the Hanford site subsurface. Incongruent dissolution of 2:1 layer-type silicates results in the formation of nitrate-sodalite, nitrate-cancrinite and zeolite X with molar Si/Al ratios close to unity during precipitation of clay-derived Si with STWL-derived Al, NO$_3$ and OH. The rate of feldspathoid and zeolite accumulation, measured using XRD, FTIR and NMR, increases with decreasing initial concentration of Cs and Sr in Mt and II. The solids exhibit increasing crystallinity and decreased susceptibility to dissolution in acidic solutions with increased aging time in STWL.

NMR data indicate that the neoformed solids comprise dominantly tetrahedrally-coordinated Al [$\text{Al}^{IV}$] that contributes to the development of high structural charge densities and, therefore, the potential for sequestration of cationic Sr and Cs. Uptake of Sr and Cs into these precipitates depends on the rate...
at which the solids are produced and the relative affinity of radionuclide contaminants for the parent clay vs. the product solids. In illite systems, FES exhibit a high affinity for Cs, removing it from solution at low and intermediate concentrations, whereas Sr was sorbed to secondary solids. Vermiculite is an effective sorbent for both Cs and Sr such that these ions are not detectable in the neoformed solids, and initial concentrations of these contaminants have no effect on mineral transformation rate. In contrast, montmorillonite exhibits the highest dissolution rate of the three clays, Cs and Sr concentrations strongly impact montmorillonite transformation rate, and both ions are found in association with neoformed solids.

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