Aluminum Effect on Dissolution and Precipitation under Hyperalkaline Conditions: II. Solid Phase Transformations

Nikolla P. Qafoku,* Calvin C. Ainsworth, James E. Szecsody, David L. Bish, James S. Young, David E. McCready, and Odeta S. Qafoku

ABSTRACT

The high-level radioactive, Al-rich, concentrated alkaline and saline waste fluids stored in underground tanks have accidentally leaked into the vadose zone at the Hanford Site in Washington State. In addition to dissolution, precipitation is likely to occur when these waste fluids contact the sediments. The objective of this study was to investigate the solid phase transformations caused by dissolution and precipitation in the sediments treated with solutions similar to the waste fluids. Batch experiments at 323 K were conducted in metal- and glass-free systems under CO₂ and O₂ free conditions. Results from X-ray diffraction (XRD), quantitative X-ray diffraction (QXRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and energy dispersive X-ray fluorescence spectroscopy (EDXRF) indicated that significant solid phase transformations occurred in the sediments contacted with Al-rich, hyperalkaline, and saline solutions. The XRD and QXRD analyses confirmed that smectite and most likely biotite underwent dissolution. The SEM and the qualitative EDS analyses confirmed the formation of aluminosilicates in the groups of cancrinite and probably sodalite. The morphology of the aluminosilicates secondary phases changed in response to changes in the Si/Al aqueous molar ratio. The transformations in the sediments triggered by dissolution (weathering of soil minerals) and precipitation (formation of secondary phases with high specific surface area and probably high sorption capacities) may play a significant role in the immobilization and ultimate fate of radionuclides and contaminants such as Cs, Sr, and U in the Hanford vadose zone.

Millions of liters of high-level radioactive waste fluids (HLWF) were produced in the U and Pu production plants during the cold war. Approximately 60% of that waste is now stored in 177 underground tanks at the Department of Energy’s (DOE’s) Hanford Site in Washington State. Of particular interest are the single shell HLWF Tanks that received REDOX wastes treated with solutions similar to the Hanford Site in Washington State. In addition to dissolution, precipitation is likely to occur when these waste fluids contact the sediments. The objective of this study was to investigate the solid phase transformations caused by dissolution and precipitation in the sediments treated with solutions similar to the waste fluids. Batch experiments at 323 K were conducted in metal- and glass-free systems under CO₂ and O₂ free conditions. Results from X-ray diffraction (XRD), quantitative X-ray diffraction (QXRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and energy dispersive X-ray fluorescence spectroscopy (EDXRF) indicated that significant solid phase transformations occurred in the sediments contacted with Al-rich, hyperalkaline, and saline solutions. The XRD and QXRD analyses confirmed that smectite and most likely biotite underwent dissolution. The SEM and the qualitative EDS analyses confirmed the formation of aluminosilicates in the groups of cancrinite and probably sodalite. The morphology of the aluminosilicates secondary phases changed in response to changes in the Si/Al aqueous molar ratio. The transformations in the sediments triggered by dissolution (weathering of soil minerals) and precipitation (formation of secondary phases with high specific surface area and probably high sorption capacities) may play a significant role in the immobilization and ultimate fate of radionuclides and contaminants such as Cs, Sr, and U in the Hanford vadose zone.

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Abbreviations: DOE, Department of Energy; EDS, energy dispersive spectroscopy; EDXRF, energy dispersive X-ray fluorescence spectroscopy; FESEM, Field Emission Scanning Electron Microscopy; HLWF, high-level radioactive waste fluids; IS, ionic strength; QXRD, quantitative X-ray diffraction; SEM, scanning electron microscopy; XRD, X-ray diffraction.
different chemical formulae, sodalite and cancrinite, which are formed in Si, and aluminate-rich caustic systems have identical chemical stoichiometry (\(Na_8Al_{24}Si_{12}O_{72}X_2\)), where \(X\) can be \(\frac{1}{2}CO_3\), \(\frac{1}{2}SO_4\), Cl, OH, or NO\(_3\) (Barnes et al., 1999a). The formation of nitrate–sodalite (Buhl and Lons, 1996) and nitrate–cancrinite (Bickmore et al., 2001) is possible in NO\(_3\)-rich systems.

The transformation of the initial solid phase because of dissolution and precipitation under hyperalkaline and hypersaline conditions is an important area of research that warrants further investigation. To understand the extent and dynamics of dissolution and precipitation in these systems, batch reactors were used to investigate interactions between Hanford sediments and Al-rich, hyperalkaline, and saline solutions similar to some tank waste fluids. The morphology of the Al-bearing secondary phases was studied for different initial Al concentrations in the contact solution and different Si/Al aqueous concentration ratios created in the soil solution during the experiments because of dissolution and precipitation reactions. The solid phase transformations that occurred in the Hanford sediments when they were contacted with Al-rich, newly formed aluminosilicates (feldspathoids and other minerals) were characterized using different techniques.

**MATERIALS AND METHODS**

**Sediments**

The fine sand and fine sandy silt sediments used in the batch experiments were collected near the 200 Area at the DOE’s Hanford Site in Washington State. These sediments are dominated by quartz (30–80%) and plagioclase feldspar (5–20%), with minor amounts (<10%) of potassium feldspar and amphibole. The clay fraction (<2 \(\mu\)m) is dominated by four clay minerals: illite (mica, 15–40 wt. %), smectite (30–40 wt. %), chlorite (15–20 wt. %), and kaolinite (<10 wt. %), with minor amounts of quartz, feldspar, and amphibole (5–10 wt. %) (Serne et al., 2001).

**Batch Experiments with Hanford Sediments**

The full description of how the batch experiments were conducted is given in the previous paper (Qafoku et al., 2003). Briefly, we conducted two similar experiments with the same solutions. The first experiment had 20 treatments: 4 Al concentrations (0.055, 0.11, 0.165, and 0.22 mol L\(^{-1}\)) by 5 time periods (3, 7, 14, 21, and 42 d), and the second one had 36 treatments: 4 Al concentrations by 9 time periods (20 min, 1, 2, 4, 8, 16, 24, 36, and 48 h). The background solution was 1 mol L\(^{-1}\) NaOH and NaN\(_3\). Both these experiments are hereafter referred to as the Batch 1 study. Because of the coarse nature of these sediments (the fine fraction makes only 1–2% of the total sediment’s mass) another similar study was conducted during this investigation to produce the necessary amount of posttreatment sediments needed for different analyses of the solid phases. A treatment with high concentrations of base and Al (4 mol L\(^{-1}\) NaOH, 0.88 mol L\(^{-1}\) Al, and 1 mol L\(^{-1}\) NaN\(_3\)) was also included in this latter experiment. The post-experiment analyses of the sediments were conducted after 3, 7, 14, 28, and 42 d of the experiment. These experiments were run inside a thermostat chamber where the temperature was kept at 323 K for the duration of the experiment. The sediments of all treatments were washed twice with DI-water over Buchner-funnel–like containers to wash out the excess salt, and were subsequently air-dried and used in postexperiment analyses.

**Characterization of Precipitates**

The air-dried reacted sediments were analyzed by powder XRD, ultra-high performance field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDS), and energy dispersive X-ray fluorescence (EDXRF). The X-ray diffraction measurements of the sediments at the end of the Batch 1 experiments were performed using a Philips X’Pert MPD system that employs a PW3050/10 vertical theta goniometer and a PW3073 ceramic X-ray tube, with a Cu X-ray source operated at 45 kV and 40 mA (1.8 kW). Powdered specimens from the <53 \(\mu\)m fraction were mounted in cavity-type sample holders and measured across 2° to 60° 26. The scan rate was 0.02°/2s, except for the untreated sample’s sample and the 21-d sample were scanned at 0.02°/5s and 0.02°/20s, respectively. The slower scan rate of 0.02°/5s was utilized for the untreated sample to firmly establish the baseline composition of the soil. The very slow scan rate of 0.02°/20s was utilized for the sample collected after 21 d of the experiment to increase the chances of observing the characteristic diffraction patterns of cancrinite and possibly sodalite. Data were analyzed using Jade (Materials Data, Livermore, CA) for matches with the Powder Diffraction File database (PDF-2, 2001 Release, International Centre for Diffraction Data, Newtown Square, PA).

Mineral abundances were determined by quantitative powder X-ray diffraction (QXRD) methods with a Siemens D-500 diffractometer using Cu-K\(_\alpha\) radiation and a Kevex PSi(Li) solid state detector. Data were obtained on samples that were ground to <5 \(\mu\)m in an automatic Brinkman Micro-Rapid agate mill. As only small amounts of sample were available, samples were not mixed with an internal intensity standard, such as corundum. The quantitative mineralogy was determined on a weight basis using the external-standard method of Chung (1974). The accuracy of the QXRD method, particularly for feldspars and zeolites, was improved by using multireflection rather than single-reflection methods. Typical two-sigma uncertainties in analyses of feldspar are ±3% (absolute) at 10% concentration and ±10% at 50% concentration; for zeolites, the uncertainties are ±1% at 10%, ±3% at 40%, and ±6% at 80%. The QXRD methods have been coded into a computer program (QUANT) that accounts for analytical problems important in the analysis of tuffs, altered tuffs, and soils: e.g., correction of clinoptilolite and opal-CT for mutual overlap and use of multiple reflections to improve results for analysis of complex tectosilicates. Further details of the basic method can be found in Bish and Chipera (1987) and the methods of multireflection analysis are described in Chipera and Bish (1995). A single mica standard was used for quantitative analyses, although SEM data show the existence of at least three different micas. The powder XRD data on nitrate-cancrinite were taken from the literature (Buhl et al., 2000).

A LEO 982 FESEM system with an Oxford ISIS energy dispersive X-ray microanalysis system, and with a SiLi detector was used for scanning electron microscopy and EDS analyses. This instrument is an ultra-high performance scanning electron microscope with a resolution of 1 nm at 30 kV and 4 nm at 1 kV. We used the microanalysis system to do both qualitative and quantitative elemental analyses of the secondary minerals that were formed during the experiment, and to identify the soil minerals onto which these secondary phases precipitated.

The EDXRF, which is a rapid and sensitive method for simultaneous analysis of up to 49 elements in solid samples,
was used to determine the total amount of different elements in the sediments at the end of the experiment.

**RESULTS**

**Results from X-ray Diffraction and Quantitative X-ray Diffraction**

The XRD patterns taken from the samples of the Batch 1 study showed the presence of quartz, albite, Ca-rich albite, orthoclase, actinolite, magnesiohornblende, clinochlore (chlorite), micas (muscovite and biotite), smectite, and calcite in the Hanford sediments (Fig. 1 and 2). Because the dissolution rate was higher in the 0.055 mol L\(^{-1}\) Al treatment as compared with the other ones (0.11, 0.165, and 0.22 mol L\(^{-1}\) Al) of the Batch 1 study, the XRD patterns of the sediments (after 42 d) of only this treatment were presented in Fig. 1. The XRD patterns collected in the other treatments were similar. Although all minerals present in the sediments should have undergone some base-induced dissolution contributing to the amounts of Si, K, Fe, and other elements released into the soil solution, no significant differences were observed in the intensities of the characteristic diagnostic maxima of the primary phases present in the sediments before and after treatment with the 0.055 mol L\(^{-1}\) Al, 1 mol L\(^{-1}\) NaOH, and 1 mol L\(^{-1}\) NaNO\(_3\) solution (Fig. 1).

The effect of base-induced dissolution was more visi-
ble in the case of relatively minor phases that were present in the sediments (Fig. 2). The patterns taken from the air-dried untreated and treated sediments with the 0.055 mol L\(^{-1}\) Al solution after 3 d of the experiment showed that the peaks between 5 and 6°2θ (~15 Å) disappeared in the latter pattern, which confirmed that smectite underwent dissolution in the first 3 d of the experiment, serving as an initial source for Si and possibly Fe released into the soil solution. This was also confirmed from the XQRD results conducted with the sediments treated with the 1 mol L\(^{-1}\) NaOH, 0.22 mol L\(^{-1}\) Al, and 1 mol L\(^{-1}\) NaNO\(_3\) solution. The most important change determined with XQRD was the significant decrease in the amount of smectite in the sample taken after 7 d of contact time (11.4%) as compared with the untreated sample (18.4%). The biotite content also decreased from 15.5% in the untreated sample to 11.8% in treated sample. It also appears that reaction changed the interlayer chemistry of smectite, collapsing some of the interlayers. Clinohlore was much more resistant to weathering and the characteristic maxima of clinohlore persisted in all the patterns. While other minerals that are present in the clay- and silt-size fraction may have also undergone dissolution, the diagnostic peaks of biotite appeared less intense in the treated materials as compared with untreated ones (Fig. 2). The scanning electron microscopy (SEM) micrographs that will be presented later in this paper showed clear signs of the OH attack on mica edges and the mica sheets were separated from one another (Fig. 5j).

The overlaid X-ray diffractograms of the untreated sediments and the sediments treated with a solution of 0.88 mol L\(^{-1}\) Al, 4 mol L\(^{-1}\) NaOH, and 1 mol L\(^{-1}\) NaNO\(_3\) showed only small variations after 7 d (Fig. 3a and b). However, these patterns did clearly show the presence of NO\(_3\)-cancrinite in the treated sediments. The main identification peak for nitrate–cancrinite is that occurring at 3.24 Å (Barnes et al., 1999b). The peaks at the d-spacing 6.3353 (13.97°2θ), 3.6589 (24.31°2θ), and 3.2393 Å (27.51°2θ) are clearly more intense in the posttreatment sample. It should be added here, however, that some of the characteristic peaks of nitrate–cancrinite were missing or were less intense than the peaks reported for NO\(_3\)-cancrinite, e.g., the peaks at 4.6906 Å (18.90°2θ), 2.7439 Å (32.61°2θ), and 2.4255 Å (37.03°2θ) (Buhl et al., 2000).

The diagnostic maxima of gibbsite, or any other Al pure phases, were not observed in the XRD patterns of the posttreated sediments. However, the Jade software used to find matches from the database suggested the formation of zeophyllite by 42 d in the higher Al concentrations (0.165 and 0.22 mol L\(^{-1}\) Al) (Fig. 4). The phase transformation of biotite to hydrobiotite as a result of the base attack on mica edges was also suggested from matching the XRD patterns from our experiments with those in the Jade database (Fig. 4). There was only a small increase in the amount of hematite determined with XQRD (from 0.1 to 0.7%), in the sample taken after 7 d of contact time with the 0.88 mol L\(^{-1}\) Al, 4 mol L\(^{-1}\) NaOH, and 1 mol L\(^{-1}\) NaNO\(_3\) solution as compared with the untreated sample. This perhaps accounted for the large change in color observed in the “after treatment” sample.

### Scanning Electron Microscopy and Energy Dispersive Spectroscopy Results

In contrast to the untreated sediment (Fig. 5a), the sediments treated with the 0.055 mol L\(^{-1}\) Al alkaline solution (Batch 1 study) were coated with secondary precipitates after 3 d (Fig. 5b). A closer look at the secondary phases formed in the first 3 d of the experiment revealed the existence of two different minerals (Fig. 5c). The first one had a “cotton-ball”–like morphology similar to that of sodalite [Na\(_8\)Al\(_8\)Si\(_{24}\)O\(_{64}\)(NO\(_3\))\(_6\)] (Barnes et al., 1999a). The more abundant of the two had the typical yarn-like morphology of cancrinite [Na\(_8\)Al\(_2\)Si\(_{6}\)O\(_{18}\)(NO\(_3\))\(_2\)] similar to the ones reported by Bickmore et al. (2001). Although some soil mineral particles were totally covered with the nitrate–cancrinite balls after 7 d (Fig. 5d), the “cotton-ball”–like crystals were not observed in the sediments of this Al treatment after 3 d. The presence of nitrate–cancrinite became more visible after 14 and 21 d (Fig. 5e). It is interesting to notice here that the precipitate formed between 21 to 42 d had a significantly different morphology (Fig. 5f and g).

The results from the qualitative EDS analyses showed that almost all newly formed solid phases had similar chemical compositions; they were rich in Si, Al, O, and Na, and had Si/Al molar ratios of about 1. The EDS quantitative analysis confirmed that the secondary minerals were mostly formed on the surfaces of plagioclase with an average chemical composition of 72.67% Si, 15.91% Al, 6.22% Ca, 3.42% Na, 1.755% K, and 0.01% Fe. The presence of a Fe-rich precipitate with a smaller, ball-like structure (diam. < 500 nm) was also visible in Fig. 5g, but we were unable to confirm its identity with the EDS analysis because these particles were small.

When the sediments where initially treated with a 0.11 mol L\(^{-1}\) Al alkaline solution (Batch 1 study) the cancrinite balls were bigger and it appears that the cotton-ball structures of probably sodalite were also present in the sediments of this treatment after 42 d (Fig. 5h). The Fe-rich small balls were quite visible on the surfaces of the mica particles of this treatment (Fig. 5i). Because less Si was released on dissolution, much less cancrinite was formed in the 0.165 and 0.22 mol L\(^{-1}\) Al treatments after 42 d, as it is clearly shown in Fig. 5j and 5k. The cotton-ball structures were also present in these treatments after 42 d, and a third mineral with a platy morphology, which could be either zeophyllite [Ca\(_4\)Si\(_3\)O\(_{8}\)(OH, F)\(_4\)] \(_2\)H\(_2\)O or gibbsite, appears to be much more abundant in the 0.22 mol L\(^{-1}\) Al treatment (Fig. 5k) compared with other ones that had less Al in the initial contact solution.

### Results from the Energy Dispersive X-ray Fluorescence Spectroscopy Analysis

The total Si content in the sediments after 42 d of contact time increased with Al concentration from 27.9 to 31.4% (Table 1). This is consistent with the results presented in the previous paper (Qafoku et al., 2003),
where it was shown that Si release from the sediments was an inverse function of Al concentration in the soil solution. In the 0.055 mol L$^{-1}$ Al treatment, some of the Si release on dissolution remained in the soil solution at the end of the experiment, because Al was almost depleted from the soil solution after 42 d. In addition, though the precipitation of alumino-silicate secondary phases enriched the solid phase with Al, resulting in an increase in the total Al percentage in the solid phase (Table 1), this also contributed to the decrease in the total Si percentage in the solids as a result of the dilution phenomenon. The lowest Fe, K, and Ca contents were found in the sediments that were treated with the 0.055 mol L$^{-1}$ Al solution where the dissolution and precipitation were more intense, and their contents also changed slightly during the experiment.

**DISCUSSION**

The significant changes in the solid phase were confirmed from the results of the XRD, QXRD, SEM, EDS, and EDXRF analyses. It should be mentioned,
Fig. 4. X-ray diffraction patterns of treated sediments with $1 \text{ mol L}^{-1} \text{NaOH}$, $1 \text{ mol L}^{-1} \text{NaNO_3}$, and the respective Al(NO_3)_3 concentrations at 42 d (Batch 1 study).

However, that the XRD patterns and QRXD analysis of the posttreatment sediments show no significant differences in the intensities of the peaks of the primary phases present in the sediments before and after treatment. They also show that among the minor phases, clinochlore is much more resistant to weathering. But the XRD patterns confirm that smectite undergoes dissolution in the first 3 d of the experiment, serving as an initial source for Si and possibly Fe that are released into the soil solution. Biotite also undergoes dissolution.

Even though clearly seen in the SEM micrographs, the presence of cancrinite and possibly sodalite is not easily detected by XRD and not detected at all by QXRD, perhaps because their contents remain low (they represent a small mass fraction of the total sediment mass), and the detection limits for the QRXD analysis, given the above analysis conditions, are on the order of 1%. Also many diffraction peaks occur at the same d-spacing as other minerals present in much higher quantities, e.g., feldspars. Besides the patterns reported by Buhl et al. (2000) for cancrinite formed at a different temperature (473 K) from that in our experiments (323 K), we are not aware of other studies documented in the literature that would have been used to compare our results.

The SEM micrographs confirm the presence of secondary alumino-silicate coatings in the sediments by no later than Day 3 of the study. It is likely that nitrate–sodalite that is formed quite early in the experiments, i.e., in the first and second day, is then probably transformed to nitrate–cancrinite via a solution mediated phase transformation reaction, i.e., sodalite undergoes dissolution and reprecipitates in the form of nitrate–cancrinite (Barnes et al., 1999a). This is probably the reason why sodalite is not observed in the samples collected after 3 d in the 0.055 mol L$^{-1}$ Al treatments. It appears that in other treatments sodalite does not undergo dissolution, probably because of the higher Al concentrations in the contact solutions of these treatments, which is shown in the previous paper to inhibit dissolution by decreasing the free OH concentration in the contact solution and by inhibition (Qafoku et al., 2003). The aqueous Si/Al molar ratio appears to have affected significantly the morphology of the newly formed alumino-silicates. This ratio remains in the range 0.096 to 0.284 during the time period of 21 d in the Batch 1 study, which means that Al is present in much greater concentrations than Si. During this time nitrate–cancrinite’s balls are quite visible as coatings on the sediments’ surfaces. Barnes et al. (1999a) and Bickmore et al. (2001) conducted experiments with the Si/Al molar ratio of 0.0599 and 0.7875, respectively, and reported similar results. The situation changes after 21 d in our study, and the aqueous molar Si/Al ratio reaches the highest value of 14.17 after 42 d, as it is discussed in the previous paper (Qafoku et al., 2003). This change in the Si and Al composition of the soil solution appears to have drastically affected the morphology of the newly formed precipitates, from the ball-like to the rod-like structures (Fig. 4f and g). It is likely that the rod-like precipitates that are formed after 21 d cover the nitrate–cancrinite balls that are formed before 21 d because the balls are still visible.

Data from these experiments were modeled using GMIN, which is a chemical equilibrium program that uses a free-energy minimization approach (Felmy, 1995). The free-energy models incorporated in GMIN include the Pitzer equations that may be successfully used to model experimental data collected from experiments conducted with highly concentrated solutions. The aqueous phase of the low Al treatments (which had 0.055 and 0.11 mol L$^{-1}$ Al in the contact solutions) was oversaturated with respect to cancrinite. This situation
was different only in the treatment that had a 0.055 mol L\(^{-1}\) Al contact solution. After 42 d, the solution was undersaturated with respect to cancrinite in this treatment. The aqueous phase of the other treatments (which had 0.165 and 0.22 mol L\(^{-1}\) Al in the contact solutions) was oversaturated with respect to both cancrinite and gibbsite.

The presence of these secondary minerals in the after treatment sediments may have a significant effect in the immobilization and ultimate fate of radionuclides and contaminants, like Cs, Sr, and U, which are present in the vadose zone sediments at the Hanford Site. These minerals possess higher specific surface area than the minerals that are initially present in the Hanford sediments. Sodalite and cancrinite are both feldspathoids with structures similar to zeolite. The structures of the minerals in the cancrinite group are characterized by stacking of six-membered rings, which gives rise to large continuous channels that are amongst the largest channels known to occur in the mineral structures (Hassan, 1997). These are also called *reservoir minerals* because of their large cation exchange capacity (Buhl and Lons, 1996) and surface sorption capacities. In addition to providing the mineral with a higher specific surface area,
Fig. 5. (a) Scanning electron micrograph taken in the untreated sediments; (b and c) Batch 1, 3 d: treated sediments with 1 mol L$^{-1}$ NaOH, 1 mol L$^{-1}$ NaNO$_3$, and 0.055 mol L$^{-1}$ Al(NO$_3$)$_3$ solution: the Si/Al aqueous molar ratio was equal to 0.121; (d) Batch 1, 7 d: the Si/Al aqueous molar ratio was equal to 0.096; (e) Batch 1, 21 d: the Si/Al aqueous molar ratio was equal to 0.284; (f and g) Batch 1, 42 d: the Si/Al aqueous molar ratio was equal to 14.17; (h and i) Batch 1, 42 d: sediments treated with 1 mol L$^{-1}$ NaOH, 1 mol L$^{-1}$ NaNO$_3$, and 0.11 mol L$^{-1}$ Al(NO$_3$)$_3$ solution: (h) cancrinite and probably sodalite crystals, and (i) a mica particle and the Fe-rich small ball crystals; (j) Batch 1, 42 d: treated with 1 mol L$^{-1}$ NaOH, 1 mol L$^{-1}$ NaNO$_3$, and 0.165 mol L$^{-1}$ Al(NO$_3$)$_3$ solution: cancrinite, probably sodalite, and zeophyllite crystals; (k) Batch 1, 42 d: treated with 1 mol L$^{-1}$ NaOH, 1 mol L$^{-1}$ NaNO$_3$, and 0.22 mol L$^{-1}$ Al(NO$_3$)$_3$ solution: cancrinite, probably sodalite, and zeophyllite crystals.

The morphology of the newly formed solid phases may take part in the structure of these secondary phases when they are formed in the sediments. As an example, the cages host a complex distribution of extra-framework cations and anions (Ballirano et al., 2000). It is possible, therefore, that contaminants and radionuclides may take part in the structure of these secondary phases when they are formed in the sediments. As an example, Se has been introduced into the cancrinite matrix by hydrothermal methods to form red-brown hexagonal crystals (Lindner et al., 1996).

The morphology of the newly formed solid phases appears to be a function of Si/Al molar ratio in the soil.
Table 1. Element concentrations in the treated sediments of the Batch 1 study after 42 d.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Initial Al conc., mol L⁻¹⁻¹</th>
<th>%</th>
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<tr>
<td></td>
<td>0.055</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>27.9 (1.4)†‡</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>4.04 (0.2)</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>8.96 (0.52)</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>1.188 (0.06)</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>2.55 (0.13)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>29.8 (1.5)</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>4.05 (0.2)</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>9.46 (0.54)</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>1.307 (0.066)</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>2.66 (0.14)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.165</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>29.4 (1.5)</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>4.1 (0.21)</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>7.87 (0.47)</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>1.308 (0.066)</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>2.78 (0.14)</td>
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</tr>
<tr>
<td></td>
<td>0.22</td>
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</tr>
<tr>
<td>Si</td>
<td>31.4 (1.6)</td>
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</tr>
<tr>
<td>Fe</td>
<td>4.21 (0.21)</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>8.08 (0.49)</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>1.404 (0.071)</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>2.94 (0.15)</td>
<td></td>
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† Average of at least two measurements.
‡ Standard deviation.

solution and microzones with different ratios probably occur in the sediments. It is quite likely, therefore, that the formation of morphologically different secondary phases will increase the physical heterogeneity in the Hanford sediments, which in turn may significantly affect contaminant mobility.

The presence of Fe precipitates is also suggested from the QXRD results and SEM micrographs, which indicates that Fe precipitates alone in pure Fe secondary phases. The relatively small balls of Fe-rich precipitates (diam. approximately 300–500 nm) are abundant on mica surfaces (Fig. 4j). Quite possibly Fe(II) is released from micas on their dissolution, and subsequently is oxidized to Fe(III) by residual O₂ or any other oxidant, and then precipitates immediately under hyperalkaline conditions.

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