

## **IMMOBILIZATION OF RADIONUCLIDES IN THE HANFORD VADOSE ZONE BY INCORPORATION IN SOLID PHASES**

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### ***Background***

The production and extraction of Pu, U and other strategic elements from irradiated uranium fuels has been a major component of the DOE mission since the early 1940's. These activities occurred at a number of DOE facilities including Hanford, Idaho National Engineering Laboratory (INEL) Los Alamos National Laboratory (LANL), Oak Ridge National Laboratory (ORNL), Sandia National Laboratory (SNL), and the Savannah River Site (SRS). At the Hanford site, the fluids resulting from extraction of spent fuel rods from 9 nuclear reactors were stored in 177 underground tanks during the period of 1944 to 1990, in areas known as "tank farms". The chemical extraction processes employed at the Hanford site varied with time, and thus composition of the tank fluids is varied. These procedures will be discussed in greater detail below, but suffice it to say here that three dominant processes were utilized during the period of active fuel reprocessing. Whereas, the complete chemical extraction and purification procedures varied for each of these processes, they had some common features. Typically, processing was initiated by dissolution of the Pu and U containing materials in nitric acid followed by eventual neutralization of the acidity (typically with NaOH) and transfer of the spent fluids to the underground tanks for storage. Thus, the high level waste (HLW) fluids that were present in many of the tanks contained large concentrations of NaNO<sub>3</sub> (often > 1 mol L<sup>-1</sup>) and hydroxyl ions, with pH values > 10 common and some in excess of 14. Many of these tank fluids also contained large concentrations of dissolved Al (which presumably stayed in solution as aluminate ions and possibly aluminate polymers) quantities of unrecovered U and Pu, numerous fission daughter products, organic ligands (from the extraction and purification processes), and a number of other inorganic ions.

One hundred and forty-nine out of the 177 waste tanks located in the Hanford Tank Farm were constructed with single walls and are commonly referred to as single shell tanks (SST). Sixty-seven of the SSTs are known or thought to have leaked, allowing from 1,920,000 to 3,456,000 L of waste fluids to migrate into the underlying vadose zone. The actual composition of these leachates is not known but the data detailed below, indicate that many of these fluids were highly alkaline (pH values > 13), and that many contained large concentrations of dissolved NaNO<sub>3</sub> and Al(OH<sub>4</sub>)<sup>-</sup> as well as substantial quantities of <sup>137</sup>Cs, <sup>60</sup>Co, <sup>90</sup>Sr, <sup>99</sup>Tc, <sup>234,238</sup>U, and other radioactive elements. Upon reaction with the underlying soil and sedimentary matrix this situation will potentially result in the formation of a number of complex precipitates that could incorporate radioactive contaminant species from the tanks. Reaction of the tank fluids with the soil matrix should cause some dissolution of the soil minerals, releasing Si into solution, and decreasing pH. These solution conditions should promote the formation of Al- and Si-

hydroxide gels, hydrotalcites, and ultimately Al-(hydr)oxides. The potential for zeolite formation may also be present. All of these potential phases have high surface reactivities, and should serve as strong sorbents and/or coprecipitates for contaminant ions present in the leachate (Cs, Co, Sr, Tc, U, etc.). Additionally, partial dissolution of the ambient soil minerals and precipitation of these secondary solids could result in significant alteration to the porosity and flow paths of the surrounding porous media. When coupled together, these chemical and physical transformations should result in dramatic changes in the fate and transport of the contaminant ions associated with tank fluids. Clearly, more information is needed before an understanding of the complex geochemical environment in the vadose zone beneath the Hanford tanks is attained.

In this three-year collaborative project, we propose to study the incorporation of representative contaminant species (Cs, Co, Sr, Tc, and U) in carefully controlled model systems to gain a more fundamental understanding of sorption, neoformation, precipitation, and exchange processes that might immobilize these contaminants in solid matrices impacted by alkaline tank fluids. These ions are present as major contaminants at the Hanford site, and have been found in plumes originating from the Hanford Tank Farm. The aqueous speciation of these ions under different solution conditions is reasonably well known, and we and others have studied their sorption behavior on a variety of oxide and oxyhydroxide surfaces under a range of environments. Thus, we have a good knowledge of their modes of sorption. However, there is a dearth of information about the conditions leading to their desorption or incorporation into insoluble solids, as discussed above. Furthermore, very little is known about the effect of aging on the stability of metal ion sorption complexes in these systems, yet it is likely that aging will produce significant changes in the sorbed contaminant species, based on findings from the small number of molecular-scale studies on changes in these species as a function of time in laboratory simulations.

### ***Specific objectives***

*We propose to investigate (1) the effect of aging on the stability of sorption complexes on Al-oxide and Al-oxyhydroxide surfaces formed from neutralization and homogeneous nucleation of alkaline aluminate solutions; (2) the sorption/coprecipitation of these elements in solids formed from reaction of alkaline aluminate solutions with simple systems of representative minerals and mineral coatings found in the soils and sediments underlying the Hanford Tank Farm (e.g., quartz, feldspars, biotite, muscovite, chlorite, clay mineral, augite, hornblende, ilmenite, magnetite, hematite, Fe(III)-oxyhydroxides, and Mn(IV)-(hydr)oxides); and (3) the sorption/coprecipitation of these elements in solids formed from reaction of alkaline aluminate solutions with soil and sediment samples obtained from the Hanford site. (4) To couple these laboratory studies to precipitation processes occurring in the Hanford vadose zone beneath the Tank Farm, we also propose to characterize the particle coatings and precipitate phases in core samples from this zone. These investigations will utilize X-ray Absorption Fine Structure (XAFS) spectroscopy, vibrational spectroscopy, NMR spectroscopy, electron and X-ray microprobe analyses, transmission electron microscopy, X-ray photoelectron spectroscopy, and other characterization studies of the speciation and spatial distribution of these ions in several model systems chosen to simulate the natural systems.*

### ***Research Tasks:***

- Task 1 is examining the interactions of contaminant ions with mono- and polymeric aluminate species, hydroxy-Al gels, and Al-(hydr)oxides that form during the neutralization of caustic Na-aluminate solutions. Spectroscopic methods will be used to determine the solid phase speciation of the Co, Cs, Sr, Tc and U in these systems. These experiments will address reactions that can potentially retard Co, Cs, Sr, Tc and U, as tank leachates interact with the underlying sediments in the absence of substantial concentrations of dissolved Si (i.e. only from the formation of Al-containing precipitates).

To date, we have prepared a range of homogeneous samples with tank simulant solutions containing NaOH (2 to 5 mol L<sup>-1</sup>) 0.1 to 1 mol L<sup>-1</sup> Al(NO<sub>3</sub>)<sub>3</sub>, and 1 to 3 mol L<sup>-1</sup> NaNO<sub>3</sub>. Samples have been prepared in Ar(g) filled glove boxes to exclude CO<sub>2</sub>. These solutions contain from 0 to 10<sup>-3</sup> mol L<sup>-1</sup> Na<sub>2</sub>CrO<sub>4</sub>, 0-10<sup>-3</sup> mol L<sup>-1</sup> CsNO<sub>3</sub>, 0 to 10<sup>-5</sup> mol L<sup>-1</sup> Co(NO<sub>3</sub>)<sub>2</sub> and Sr(NO<sub>3</sub>)<sub>2</sub>, and 0 to 10<sup>-3</sup> mol L<sup>-1</sup> UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>. The Co, Sr, Cs and U have been added to separate solutions. Subsets of these samples have also been prepared in the presence of carbonate ions by the addition of 10<sup>-5</sup> to 10<sup>-3</sup> mol L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub>. The samples have been maintained in sealed HDPE bottles, at 50°C.

Analyses of these materials has included ICP-OES and ICP-MS measurements of solution composition, as well as powder x-ray diffraction, SEM, FTIR, Al-NMR and Al, Co and Sr XAS on selected samples.

- Task 2 is examining the interactions of tank simulants (of the same composition as in Task 1) with model silicate minerals. These include x-ray amorphous silica, a model K-feldspar from the Stanford mineral collection and uncontaminated Hanford sediments. Analyses as described above have been conducted on selected samples.
- Task 3 is exploring the effects of tank simulants on the transport of selected contaminant ions (Cs and Cr) in sediment samples obtained from the Hanford formation.

Design of 1-D transport studies: a) 6 flow experiments varying NaOH, KNO<sub>3</sub>, and NaNO<sub>3</sub>, b) maximize leaching by fast flow over long time period through columns (1600 pore volumes), and 50°C. Measure: a) Si, Al in effluent, changes in bulk density and porosity, changes in sorption of Cs and CrO<sub>4</sub> for untreated and 6 different treatments.

- In Task 4, we will carry out detailed geochemical, mineralogical and spectroscopic characterization of contaminated sediments that will be obtained from areas impacted by tank plumes. These materials will be complex and many may be potentially hazardous, thus some of our analyses will be constrained by safety considerations. However, we will still be able to conduct detailed investigations of these materials at PNNL and some may be suitable for further examination off site (i.e. at DOE synchrotrons). We are presently collaborating on the analyses of sediments collected

from the slant bore hole recently drilled under SX 108 at the Hanford site. We will be conducting XAS studies on these samples in January of 2001 at the Stanford Synchrotron Radiation Laboratory.

## Results

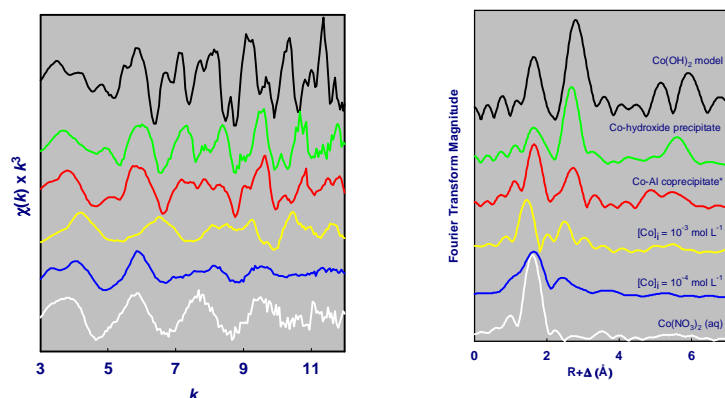
### Task 1

Aluminum hydroxide  $[\text{Al}(\text{OH})_3]$  was precipitated from reaction of 1M  $\text{Al}(\text{NO}_3)_3$  and 5 NaOH solution. When NaOH concentration was  $>3.0\text{M}$  (mole ratio of  $\text{OH}^-$  and  $\text{Al}^{3+}$  is  $> 3:1$ ),  $\text{Al}(\text{OH})_3$  was crystallized in the form of gibbsite and bayerite (as indicated by XRD, FTIR, Al-NMR and Al-XANES; data not shown). The total amount of precipitation decreased as NaOH concentration increased. The greater the NaOH concentration, the more  $\text{Al}^{3+}$  remained in the solution phase. Bayerite tended to form in relatively lower (3.0-3.5M) NaOH concentration. All sample pHs remained high, around 13.0-13.5. When the mole ratio of  $\text{OH}^-$  to  $\text{Al}^{3+}$  was  $< 3:1$ , the alkaline aluminate solution produced gel-like materials, probably amorphous aluminum (hydr)oxide polymer. These are presently being analyzed by Al-NMR. Almost all ( $>98\%$ ) Al was solidified; very little amount of Al was detected in the solution phase. The pH dropped to around 5-6 in these samples. Addition of  $\text{Na}_2\text{CO}_3$  to these solutions enhanced the formation of bayerite in direct proportion to the total  $\text{CO}_3^{2-}$  concentration.

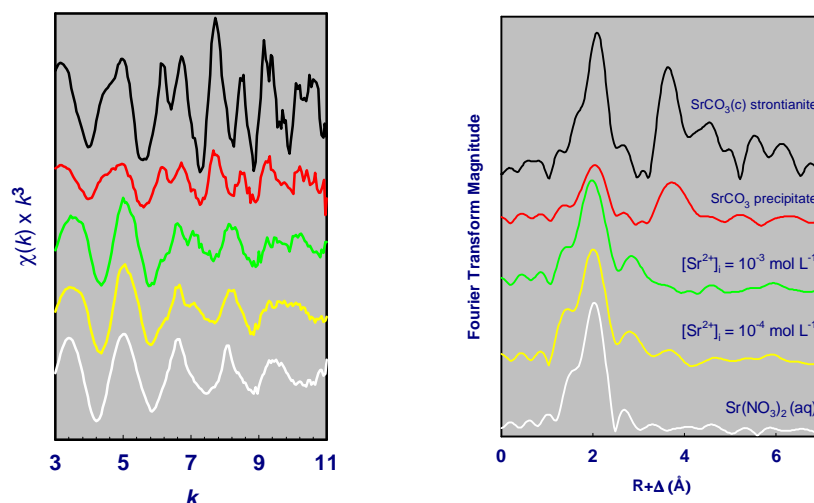
Uranium (U) concentration in the liquid phase was very low in every sample (including gel type samples), suggesting that almost all of the U was immobilized in the solid phase by sorption, coprecipitation, or precipitation. The extent of U removal from solution was independent of the quantity of  $\text{CO}_3^{2-}$  present, decreasing the likelihood of sorption as the dominant U removal mechanism. Inasmuch as the total concentration of U had no influence on the XRD patterns of gibbsite and bayerite in these samples, it is unlikely that coprecipitation with Al-hydroxides was responsible for the removal of aqueous U. Careful examination of the solids with FTIR and XRD indicated the presence of a Clarkeite-like phase.

Cs uptake in the initially homogeneous solutions is small with approximately 10% removal of Cs from solution. No effect of aging is apparent on Cs uptake, nor do Cs additions influence the composition of the Al-precipitates (gibbsite and bayerite). These samples will be examined by Cs-XAS.

Co was completely removed from solution. Sr removal was on the order of 30%. Co and Sr EXAFS on solids aged for 30 days showed unique spectra that have not been previously described in the literature.



Co EXAFS in the hyper-alkaline Al-precipitates ( $[\text{Co}^{2+}]_i = 10^{-3}$  and  $10^{-4} \text{ mol L}^{-1}$ ) are unique. \*Co-Al coprecipitate prepared near pH 7.



•Sr EXAFS in the hyper-alkaline Al-precipitates ( $[\text{Sr}^{2+}]_i = 10^{-3}$  and  $10^{-4} \text{ mol L}^{-1}$ ) are unique.

Formal analyses of these data are underway and we will examine a wider range of samples in the future.

## Task 2

Addition of amorphous  $\text{SiO}_2$  to alkaline Na-aluminate solutions resulted in the formation of gibbsite as well as a series of zeolites with the general formula of  $\text{Na}_a\text{Al}_b\text{Si}_c\text{O}_d$ . Cs uptake in these systems was much greater than in the initially homogeneous solutions. Presumably Cs uptake in these systems is due to sorption by the zeolites. XAS measurements on these systems are planned for the 2001 fiscal year.

Reaction of Hanford sediments with alkaline Na-aluminate solutions resulted in a more complex pattern of Cs uptake. Initial removal of Cs from solution was rapid. ....

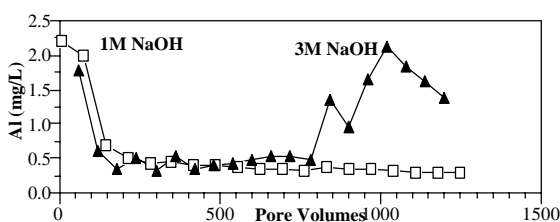
U uptake in samples containing Hanford sediments and alkaline Na-aluminate solutions was not significantly different from the samples examined under Task 1.

Heterogeneous uptake of Sr has been restricted to model experiments on Mn-oxides and the model K-feldspar. Data collection on these samples is preliminary and will be elaborated on in fiscal 2001.

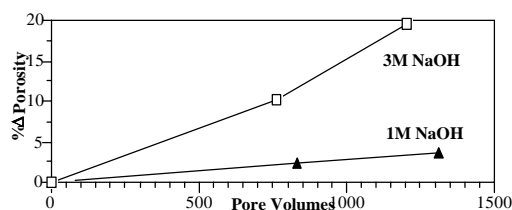
Reaction of the Hanford sediments with NaOH-NaNO<sub>3</sub> solutions and with alkaline Na-aluminate solutions resulted in a change in the sediment color from dark brown to bright red, suggesting release of Fe from Fe-containing solid phases and precipitation of Fe-(hydr)oxides.

### Task 3

In the absence of added Al in the influent solutions, significant dissolution of sediment Al occurred. Concomitant increases in porosity and decreases in bulk density were observed.



- initial Al dissolution (<50 pv) likely removes highly soluble Al phases
- 3M NaOH may be removing less soluble phases at later times (>800 pv) that were precipitating and redissolving



- a significant volume of sediment is being dissolved: porosity up 4% with 1M NaOH (bulk density down 6%) porosity up 20% with 3M NaOH (bulk density down 26%)

Aluminum solubilization and deposition in Hanford sediment columns.

### Planned Activities

Planned future activities will:

1. Continue the aging of the samples prepared in year 1, with extensive examination of the local chemical environments of Cs, U, Sr and Co by XAS.
2. Examine the potential for the reduction of U(VI) and Cr(VI) by Fe(II) released during the reaction of alkaline Na-aluminate solutions with model phases and Hanford sediments, in batch and flow-through systems

3. Begin modeling of the Al-XANES and Al-NMR data from precipitates formed in Na-aluminate solutions.
4. Examine the interfacial chemistry of U(VI) in fluids consistent with the tanks present in the Hanford B, BY and BX farms.
5. Begin analyses and XAS examination of sediment samples collected from beneath the SX tank farm at the Hanford site.