IMMOBILIZATION OF RADIONUCLIDES IN THE HANFORD VADOSE ZONE BY INCORPORATION IN SOLID PHASES
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Lead Principal Investigator:

Samuel J. Traina
School of Natural Resources
The Ohio State University
2021 Coffey Rd.
Columbus, OH 43210
(614) 292-9037
Traina.1@osu.edu

Co-Investigators:

Philip Grandinetti
Department of Chemistry
The Ohio State University
120 West 18th Ave.
Columbus, OH 43210
(614) 292-6818
Grandinetti.1@osu.edu

Gordon E. Brown, Jr.
Geological & Environmental Sciences
Stanford University
Stanford, CA 94305
(650) 723-9169
Gordon@pangea.Stanford.edu

Calvin C. Ainsworth
Interfacial Geochemistry Group
Pacific Northwest National Laboratory
P.O. Box 999, MS K3-61
Richland, WA 99352
(509) 375-2670
Calvin.ainsworth@pnl.gov

Jim E. Szecsody
Interfacial Geochemistry Group
Pacific Northwest National Laboratory
P.O. Box 999, MS K3-61
Richland, WA 99352
(509) 375-6080
Jim.szecsody@pnl.gov

Postdoctoral Researchers:

Isao Yamakawa
School of Natural Resources
The Ohio State University
2021 Coffey Rd.
Columbus, OH 43210
yamakawa.2@osu.edu

Subramanian Prasad
Department of Chemistry
The Ohio State University
120 West 18th Ave.
Columbus, OH 43210
sprasad@chemistry.ohio-state.edu

Jeff Warner
Geological & Environmental Sciences
Stanford University
Stanford, CA 94305
warner@pangea.stanford.edu

Graduate Students:

Yong-tian He
School of Natural Resources
The Ohio State University
2021 Coffey Rd.
Columbus, OH 43210
He.51@osu.edu

Jeff Catalano
Geological & Environmental Sciences
Stanford University
Stanford, CA 94305
catalano@pangea.stanford.edu

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 $NaNO_3$ (often > 1 mol L^{-1}) 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 $NaNO_3$ and $Al(OH)_4^-$ as well as substantial quantities of ^{137}Cs, ^{60}Co, ^{90}Sr, ^{99}Tc, $^{234,238}U$, 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.

Research Objectives

Specific objectives are 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, ilmentie, 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 the these ions in several model systems chosen to simulate the natural systems.

- 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

subtantial concentrations of dissolved Si (i.e. only from the formation of Al-containg precipitates

- Task 2 is examining the interactions of tank simulants (of the same composition as in Task 1) with silica and silicate minerals. These include 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 investigating the mechanisms that control the fate of Cr in the Hanford sediments with high pH, Al-rich, saline solutions similar to tank fluids chemical composition. Under alkaline conditions, hexavalent chromium [Cr(VI)] should be highly mobile in the sediments of the vadose zone underneath the tanks at Hanford site. However, recent observations of Cr transport from alkaline tanks at Hanford site indicate that Cr was indeed immobilized. Therefore, Cr(VI) may be involved in transformation processes such as reduction to Cr(III). These experiments will address the mobility of Cr in the site.

- Task 4 is carrying 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.

Research Progress and Implications

Task 1

To date, we have prepared a range of homogeneous samples with tank simulant solutions containing 1 to 5 mol L^{-1} NaOH, 0.1 to 1 mol L^{-1} Al(NO$_3$)$_3$, and 0 to 3 mol L^{-1} NaNO$_3$. Samples have been prepared in Ar(g) filled glove boxes to exclude CO$_2$. These solutions contain from 0 to 10^{-3} mol L^{-1} Na$_2$CrO$_4$, 0-10^{-3} mol L^{-1} CsNO$_3$, 0 to 10^{-5} mol L^{-1} Co(NO$_3$)$_2$ and Sr(NO$_3$)$_2$, and 0 to 10^{-3} mol L^{-1} UO$_2$(NO$_3$)$_2$. 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^{-5} to 10^{-2} mol L^{-1} Na$_2$CO$_3$. The samples have been maintained in sealed HDPE bottles, at 50°C.

Aluminum hydroxide, Al(OH)$_3$ was precipitated from reaction of 1M Al(NO$_3$)$_3$ and 5 NaOH solution. When NaOH concentration was >3.0M (mole ratio of OH$^-$ and Al^{3+} is > 3:1), Al(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 Al^{3+} remained in the solution phase in the form of Al(OH)$_4^-$. 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 OH^- to 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 Na_2CO_3 to these solutions enhanced the formation of bayerite in direct proportion to the total CO_3^{2-} concentration.

Cs uptake in the initially homogeneous solutions was small with approximately 10% removal of Cs from solution. No effect of aging is apparent on Cs uptake, nor did 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.

Mixing 10^{-3}M UO_2^{2+} solution and NaOH solution yielded a yellow precipitate identified as $Na_2U_2O_7$ (clarkeite) by X-ray diffraction. U concentration in the liquid phase was very low, indicating that > 99.5 % U was immobilized in the form of $Na_2U_2O_7$. High pH and high Na concentration make $Na_2U_2O_7$ very stable. $Na_2U_2O_7$ dissolution was observed only when the solution pH was changed to 3 to 4. In the presence of CO_3^{2-} at high pH, uranyl ion is indeed mobilized by making complexes such as carbonate, hydroxyl, and carbonato-hydroxo uranyl complexes (Barger et al., 2000; Reeder et al., 2000; Wahlgren et al, 1999; Clark et al, 1999). Yamanaka et al. (1998) reported that 0.1M CO_3^{2-}concentration resulted in $Na_2U_2O_7$ dissolution even in highly basic solution. However, the U concentration in the solution was unaffected by 10^{-4}~10^{-2}M CO_3^{2-} concentration in this system (figure 1).

Figure 1. Changes in U concentration with different carbonate concentration in 1M NaOH solution (pH 13.5). Initial U concentration was 10^{-3}M.
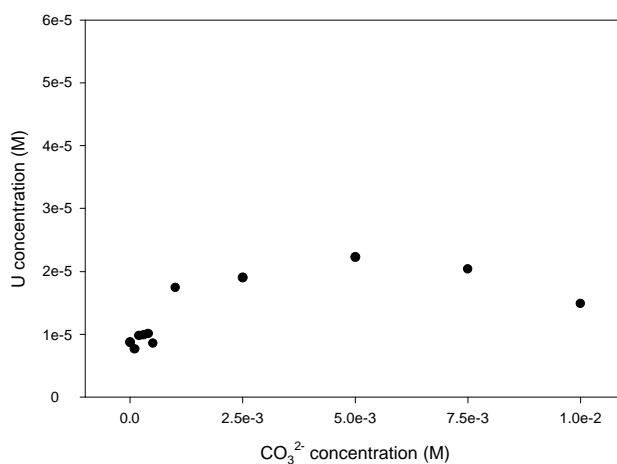
Inasmuch as the total concentration of U had no influence on the XRD patterns of gibbsite and bayerite in theses samples, it is unlikely that coprecipitation with Al-hydroxides was responsible for the removal of aqueous U. Careful examination of the solids with FTIR and XRD indicated the presence of a Clarkeite-like phase.

Formation of discrete clarkeite particles was only observed when the UO_2^{2+} concentration was high (10^{-2} M). At lower concentrations, the SEM images indicated that U was dispersed, associating with small particles of $Al(OH)_3$ (figure 2). We attemped to separate these U precipitates with high density fluids, but separation from $Al(OH)_3$ was not achieved.

Figure 2. SEM images of A) clarkeite ($Na_2U_2O_7$) and b) $Na_2U_2O_7$ on $Al(OH)_3$
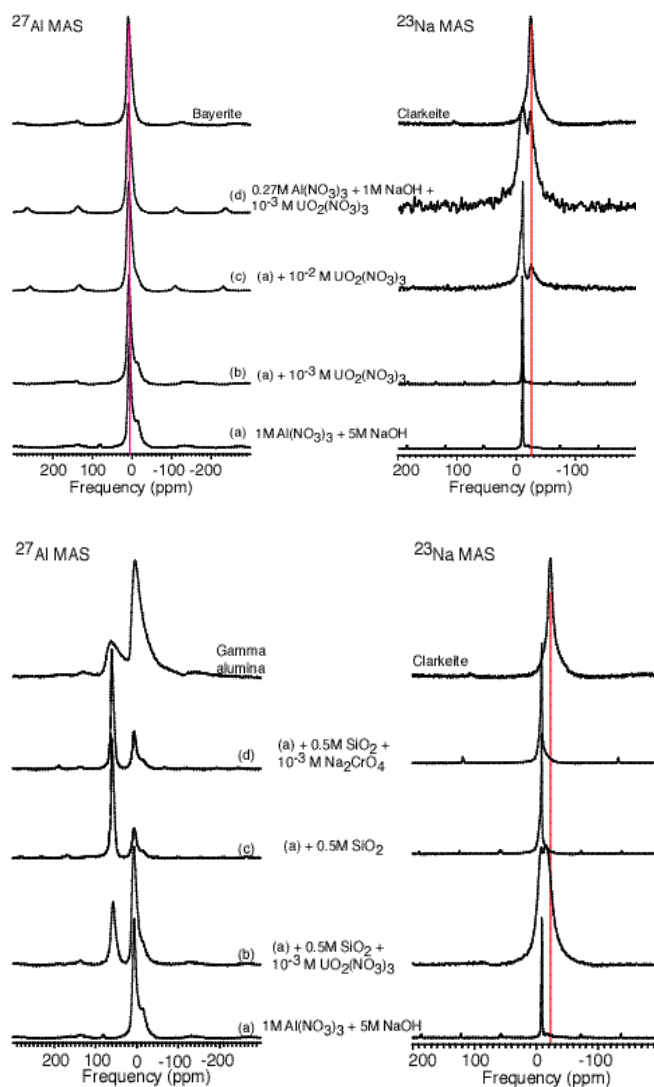
A   B
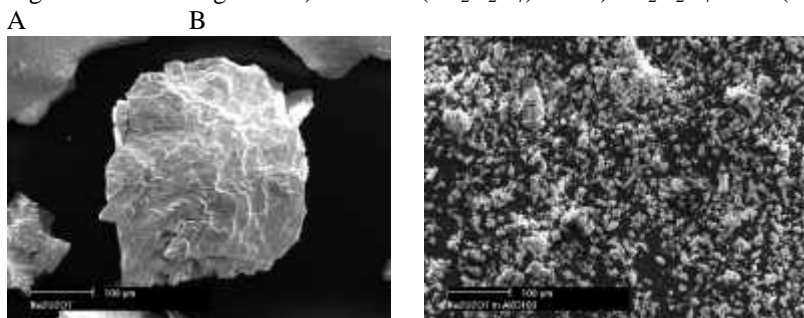
Task 2

Addition of amorphous 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 $Na_aAl_bSi_cO_d$. 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 next 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.

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 in the next fiscal year.

Reaction of the Hanford sediments with $NaOH$-$NaNO_3$ 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.

Addition of amorphous SiO_2 lowered the pH to around 10-11 because of silicic acid formation from reaction with OH^-. The aqueous concentration of U in these systems was greater (2.5×10^{-4}M, 25% of total U) possibly due to the formation of poorly crystalline clarkeite – like phases. While clarkeite could not be detected by powder XRD in these samples, EXAFS indicated a clarkeite-like coordination environment for U. Supporting evidence for the formation of clarkeite in these samples was provided by NMR as described below.

Multinuclear (^{27}Al, ^{23}Na, and ^{29}Si) techniques such as magic-angle spinning (MAS) and multiple quantum magic-angle spinning (MQ-MAS) were used to probe the nature of various species formed (figure 3). The solid obtained after freeze-drying a fluid composition of 1M $Al(NO_3)_3$ and 5M NaOH is characterized by two Al environments in the ^{27}Al spectrum and is identified as gibbsite. In the presence of added dopants (for e.g., 10^{-3} M $UO_2(NO_3)_3$), or under lower NaOH concentration, bayerite co-precipitated. Commercial bayerite shows a single resonance attributed to one crystallographic site.

However, due to the narrow range of chemical shift for octahedral aluminum and the presence of significant amount of disorder, overlapping of resonances occur. Thus, identification of different phases or mixtures there of based on observed chemical shift is difficult. Measurement of the spin-lattice relaxation rate constant (T_1) is an useful tool in such cases. The measured T_1 of gibbsite and bayerite are widely different (240 ms and 360 ms, respectively), and the T_1 for other samples (containing mixtures), fall in between. Isotropic spectra were also obtained by multiple quantum MAS spectroscopy and NMR parameters were extracted. [23]Na MAS measurements indicated, in addition to $NaNO_3$, the formation of sodium diuranate (clarkeite) in certain samples where uranium nitrate concentration was high.

In solids precipitated from gels containing SiO_2, in addition to the presence of octahedral Al sites such as observed in gibbsite and bayerite, [27]Al measurements indicated the presence of tetrahedral Al species including zeolitic aluminum. These tetrahedral sites are different from those present in gamma alumina. ^{29}Si MAS NMR measurements (not shown) corroborated the presence of Si-O-Al linkages. However, in the presence of added SiO_2, clarkeite formation was restricted.

Figure 3. [27]Al and [23]Na MAS

Task 3

To examine the adsorption and reduction of Cr(VI) on specimen biotite, we have prepared 0.1g of biotite and 40ml of the model solutions including 1 to5molL^{-1} NaOH, 1 to 3molL^{-1} Al(NO$_3$)$_3$, and 10^{-4} to 1mmolL^{-1} Na$_2$CrO$_4$. The homogeneous reduction of Cr(VI) was examined in the Fe(II) solutions including 1molL^{-1} NaOH, 1 to 3 mmol FeCl$_2$, 1 molL^{-1} NaNO$_3$. All samples were prepared in an Ar-filled glove box, in polyethylene tubes and aged for one week at 50°C.

In our high pH experiments some Cr(VI) was apparently reduced by Fe(II) very quickly and formed red-brown precipitates within seconds after mixing of the initial solutions. However, after 1 week of reaction there was still some Cr left in solution (0.44 to 0.97 mmolL^{-1}). UV-vis spectroscopy indicated that this was all in the form of Cr(VI). The quantity of Cr(VI) removal from solution increased with increased initial concentrations of Fe(II). In the absence of Cr(VI) all of the initial Fe(II) remained in solution. However, addition of 1 mmol L^{-1} Na$_2$CrO$_4$ resulted in complete removal of all detectable Fe from solution. The addition of 1 mol L^{-1} NaNO$_3$ and 0.01 mol L^{-1} Na$_2$CO$_3$ did not have a significant effect on Cr(VI) reduction.

Eary and Rai (1989) suggested that chromate was not adsorbed to biotite at high pH and Zachara and others (1988 and 1989) have shown that chromate was not adsorbed onto iron oxides at pH values greater than 11.5 to 12. However, in the present study, reaction with biotite removed from 20 to 100% of the initial Cr from solution. Figure 4 shows Cr, K-edge XANES from treatments 6 and 7 (a and b). The lack of any detectable pre-edge peak clearly indicates the conversion of Cr(VI) to Cr(III). No Cr(VI) reduction was observed in the biotite-free control. During these experiments, we observed that the bottom of the reaction vessels turned red-brown in treatments with initial Cr(VI) concentration $\leq$ 10^{-5} mol L^{-1}; this might have been due to the precipitation of an Fe(hydr)oxide as Fe originating from biotite dissolution and was oxidized by Cr(VI). Interestingly, in treatments with greater initial Cr(VI) concentration, there was no visible red-brown precipitates.
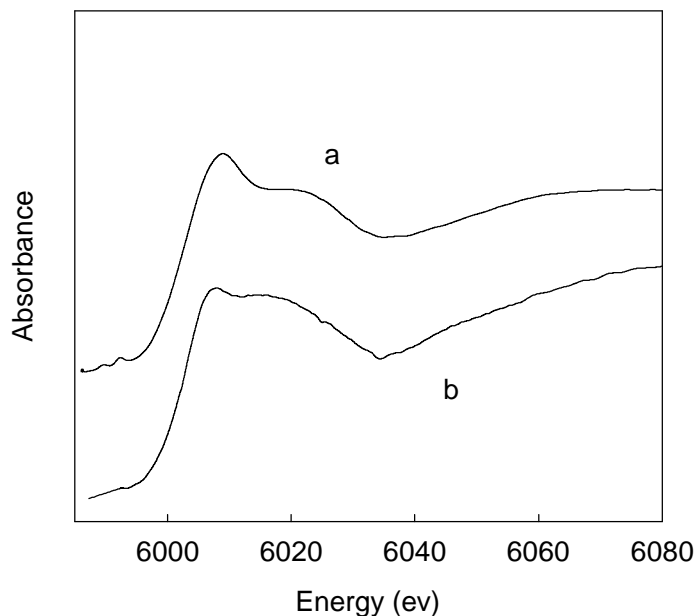

Figure 4. Cr K-edge spectra of biotite samples reacted with either a) 1 mmol L^{-1} Na$_2$CrO$_4$ or b) 100 μmol L^{-1} Na$_2$CrO$_4$, in the presence of 5 mol L^{-1} NaOH, and 1mol L^{-1}

Al(NO$_3$)$_3$.   Absence of any pre-edge peak indicates that all Cr is present as Cr(III).

It is apparent the present study that Cr(VI) reduction by biotite did occur.   In companion preliminary experiments we have observed similar patterns of Cr(VI) reduction (in the presence of 1 to 4 mol L^{-1} NaOH) in heterogeneous systems containing synthetic magnetite, a magnetic fraction separated from sediments obtained from the Hanford site and a nonmagnetic, < 200 μm size fraction of sedimentary material, also obtained from the Hanford site. Apparently alkaline induced dissolution of Fe(II) containing solids can indeed result in Cr(VI) reduction.

The capacity of clays to reduce Cr(VI) is correlated with their ferrous iron content (Taylor et al., 2000). Eary and Rai (1989) found that ferrous iron-bearing minerals such as hematite and biotite reduced hexavalent chromium as the minerals underwent dissolution, the rate of reduction was limited by the rate of Fe(II) release from the minerals. They found that the initial rate of chromate reduction is dependent on the dissolution rates of the ferrous iron contents of these minerals. However, the study of Peterson et al. (1997) suggests that reductive sorption of chromate on iron bearing minerals and "zero-valent" iron in the subsurface is a self limiting process as iron (II) is consumed on the surface, and Cr(III)-oxyhydroxide builds up on the surface. The insulating nature of these layers prevents electron transfer from deep layers, thus bringing redox processes to a halt. The extent to which this occurs in hyperalkaline solutions is not yet known.

Ilton and Veblen (1994) used XPS and SEM to study the reaction of biotites with Cr(VI) solutions, they found that Cr is strongly sorbed by the edges of mica books relative to the basal plane. In fact, much of the chromium associated with the basal plane is sorbed by steps and layer edges. In the present study, SEM images of biotite basal planes and edges did not show Cr-rich precipitates (data not shown).

It is evident from the present study that reduction of Cr(VI) by Fe(II)-containing solids can occur. While not discussed above, the reaction rates appear to increase with increasing NaOH concentration (data not shown). This may be due to base-induced dissolution of the Fe(II)-containing silicates, leading to release of Fe(II) to solution. However, it is not clear why increases in NaOH concentration would accelerate the reduction of Cr(VI) by magnetite (Fe$_3$O$_4$) yet our initial experiments suggest that this can indeed occur. The extent to which this happens in field environments (e.g. the Hanford vadose zone) is not clear, but it seems likely that Cr(VI) reduction would occur if sufficient NaOH were available for reaction with Fe(II)-containing solids. Indeed the reduced Cr was identified in field samples from the SX-108 bore-hole discussed elsewhere in this report, and it is worth noting that the most extensive reduction of Cr was found in field samples that had the greatest pH. Thus, the most critical factor in the *in situ* reduction Cr(VI) to Cr(III) by sedimentary Fe(II) may have been the presence of and persistence of hyper-alkaline solutions in the Hanford vadose zone.

Task 4

To determine the potential for the in-ground inventory of Cr to migrate as a result of future meteoric recharge or spills from tank sluicing operations, it is important to understand where it is, what are the predominate geochemical species, and what are the reactions that lead to its speciation and distribution. To date, we have been collaborating with the Hanford Science and Technology program and the Hanford Office of River Protection to investigate the solid–phase speciation of Cr, *in situ*, in sediments collected from beneath the SX-108 Tank at the Hanford site. Breifely, we used bulk XAS and XAS-microspectroscopy to study the spatial distribution and oxidation states of Cr presen in the actual sediments impacted by the tank plume.

From the few WMA S-SX sediments that have been studied, Cr is present as the reduced, cationic Cr(III) and anionic Cr(VI) species. The spatial distribution of the Cr(III) species is heterogeneously dispersed as small "hot spots". These loci of Cr(III) concentrations are often well correlated with the presence of Fe and Mn; and in several instances have been shown to be associated with biotite mica. Presumably, the Cr(III) has formed a mixed metal oxide. Chromate, on the other hand, appears to be more uniformly dispersed throughout the sediments. Extraction of Cr concomitant with Fe and Al yields reasonable correlations suggesting that the CrO_4^{2-} anion is associated with Fe and Al oxides; presumably present as weak outer-sphere surface complexes.

Assuming that the Cr loss to the vadose zone from tank leaks was initially Cr(VI), reduction of Cr(VI) occurred as the fluid was transported away from the leak source. The source of electrons for the reduction of Cr(VI) to Cr(III) is suspected to originate from several sources; the reduced Fe(II) present in the mixed valance mineral magnetite, and the reduced Fe(II) and Mn(II) in 2:1 layer-aluminosilicate minerals such as chlorite and biotite mica. All three of these minerals are present in the Hanford formation sediments; with biotite having the greatest abundance. Under the high pH, high salt, and elevated temperature conditions suspected of REDOX leaked wastes, the homogeneous reduction of Cr(VI) by $Fe(II)_{(aq)}$ is very fast, almost instantaneous. In heterogeneous system with biotite or magnetite as the only source of reductant, the rate of Cr reduction is slowed and follows biotite > magnetite. In column studies with Hanford sediments, residence time has been shown to an important element in the retardation of Cr(VI) influent; presumably because of reduction. Hence, one must surmise that the rate-controlling step in the reduction of Cr(VI) is the dissolution of Fe(II) and Mn(II) containing minerals. The reduction is followed by the rapid precipitation of mixed metal oxides, essentially at, or near the source of reductant release. This hypothesis is supported by the abundance of reduced Cr(III) and its highly heterogeneous distribution as "hot spots" of Cr(III) observed by XAS.

The high pH and elevated temperature of the tank-leaked fluids appears key to the magnitude of the Cr(VI) reduction. Under these conditions, the rate of layer aluminosilicate dissolution is substantially increased, as is the rate Fe(II) reduction of Cr. A question of a sediments reductive power, or potential, is still to be addressed. From X-ray diffraction analysis of sediments impacted by these fluids, it is clear that biotite is still present [as is Cr(VI)]; although there is a substantial decrease in smectite clays and chlorite. The apparent precipitation of redox products at or near the source of reductant release suggests that these surfaces may become passivated with time even in the presence of high OH concentrations. Hence, there appears to be a limit to the reduction potential that is well below the concentration of reductant.

Chromate is retained, only slightly if at all, by weak adsorption to secondary Al and Fe oxides at pH and ionic strength conditions of the tank-leaked fluids. Even under neutral pH conditions, the retardation of Cr(VI) was minimal at best (an $R_f < 1$). As fluid flow slowed and eventually stopped the Cr(VI) was held in place. Because of the elevated temperatures, water content decreased, and potentially, Cr(VI) fell out of solution as a soluble Na salt. Either way, one is left with a fairy uniform distribution of Cr(VI) in the sediments.

Hence, one is left with a substantial in-ground inventory of Cr in the S-SX vadose zone sediments. The stability Cr(III) oxides and its limited toxicity minimizes concern for its presence. Cause for concern, however, lies with the inventory of Cr(VI). It is unlikely that the rate of reduction will continue with meteoric recharge as the pH has moderated over time because of the aforementioned dissolution reactions and recarbonization of the high pH fluids by CO_2. The pH of all sediments is at or below 9.5 and below about sediment the SX-108 7A depth (~84 ft bgs) the pH is between 7.2 and 8.3 (typical pH values for the Hanford formation sediments). While mineral dissolution will continue, its rate will be substantially slower and Cr(VI) will have to compete with O_2 oxidation of Fe(II) and Mn(II) released. Other sources of Cr(VI) reduction (e.g., magnetite) will continue but its abundance is limited. Therefore, it must be assumed that the reactions that led to substantial reduction of Cr(VI) will be of limited value in retarding Cr(VI) in the future.

The majority of the Cr(VI) currently in the vadose zone is extremely mobile and its retardation, from the results of column studies, appears minimal. There appears to be two pools of Cr(VI) in the contaminated sediments studied to date. The largest pool is released rapidly with limited, or no retardation. The residual $NaNO_3$ from tank-leaked fluids appears to assist in the mobilization of this pool of Cr(VI). The second pool of Cr(VI) is more strongly bound to the sediments (albeit only slightly). However, it is unclear at this time whether this division into two pools is an artifact of the high ionic strength of the first few pore volumes or related to 1) the presence of a soluble Cr salt (probably Na based) versus a smaller pool of Cr weakly bound as outer-sphere complexes at oxide surfaces, or 2) different pools of Cr(VI) exhibiting different surface binding strengths.

The implications of the above discussion are clear. There is a large mobile pool of Cr(VI) that will transport with meteoric recharge or because of spills during proposed sluicing operations. It's retardation by uncontaminated sediments below will be minimal and the potential for the Cr(VI) to reach groundwater must be considered reasonable.

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 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. Identify the structure of U(VI) in the high silicate conc. solution.
5. Examine clarkeite formation on different types of solid surfaces.
6. Examine the interfacial chemistry of U(VI) in fluids consistent with the tanks present in the Hanford B, BY and BX farms.
7. Continute analyses and XAS examination of sediment samples collected from beneath the SX tank farm and the BY farm at the Hanford site.

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