

Final Report: Phase Chemistry of Tank Sludge Residual Components:

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INTRODUCTION

The US Department of Energy (DOE) has millions of gallons of high level nuclear waste stored in underground tanks at Hanford, Washington and Savannah River, South Carolina. These tanks will eventually be emptied and decommissioned. This will leave a residue of sludge adhering to the interior tank surfaces that may contaminate nearby groundwaters with radionuclides and RCRA metals. Performance assessment (PA) calculations must be carried out prior to closing the tanks. This requires developing radionuclide release models from the sludges so that the PA calculations can be based on credible source terms. These efforts continued to be hindered by uncertainties regarding the actual nature of the tank contents and the distribution of radionuclides among the various phases. In particular, it is of vital importance to know what radionuclides are associated with solid sludge components. Experimentation on actual tank sludges can be difficult, dangerous and prohibitively expensive. The research funded under this grant for the past three years was intended to provide a cost-effective method for developing the needed radionuclide release models using non-radioactive artificial sludges. Insights gained from this work will also have more immediate applications in understanding the processes responsible for heel development in the tanks and in developing effective technologies for removing wastes from the tanks.

Secondly, the DOE must constantly demonstrate progress and justify its programs to a wider audience than just the immediate technical community associated with nuclear waste issues. This research was particularly effective at fulfilling this need. The American Chemical Society selected the topic as being worthy of a press release in conjunction with its August annual meeting in New Orleans in 1999 and a published account of the state of the research at that time is included in the ACS Symposium Series Monograph. The American Association of Science (AAAS) taped an interview for their national radio news service and Channel 7 (TV) in Albuquerque also did a piece on the topic. In the popular press, the work has been written up in Environmental Health Perspectives, The Economist, and even Popular Mechanics. The Discovery Channel on-line magazine also did a piece on the subject. Finally, technical presentations of research results was also made at the Waste Management 2000 conference last February and at the Materials Research Society meeting in Boston in Nov. of 1999. Since notification of a failure to renew this grant was not received until very late in the FY only minimal funds remained for final report preparation. Thus, the balance of this report is taken from the various texts already prepared documenting the program's technical accomplishments.

RESEARCH STATUS AT THE TIME OF GRANT TERMINATION

I Artificial Sludge Synthesis

Even when wastes are subdivided according to the different fuel reprocessing technologies a large number of potential waste streams are involved. This study attempted to identify a waste stream for each process that contained the greatest amount of radioactivity, and then use that as a basis for sludge synthesis. This automatically deleted cladding wastes from consideration except when, as with the early BiPO₄ process, they were mixed with wastes from fuel reprocessing. Table 1 summarizes the results from this effort. For the BiPO₄ process the "1C/CW" waste was selected based on tabulations in Kupfer, Table C-5 (1). Redox process waste streams were approximated based on the CWR1 and CWR2 waste streams from Table D2-3 in the same source. Waste solution chemistry from U-recovery operations employing the TBP process was developed from Kupfer (1) using metal wastes from the bismuth phosphate processes (also Table C-5) variously supplemented by input from Agnew (2). PUREX wastes were derived principally from Agnew (2) with supplemental data from other sources (3, 4, 5). Early parts of this study also used a simplified "NCAW" (neutralized current acid waste) mix developed by Pacific Northwest National Laboratories to simulate late-stage PUREX processes wastes (6).

Prior to storage the acid wastes were rendered strongly caustic with NaOH and the NO₃⁻/NO₂⁻ ratio was adjusted to further minimize corrosion of the mild steel tank liners. *It is the premise of this research that the neutralization of the acid wastes was the step which fixed the phase chemistry of the sludges.* Thus, the first step in artificial sludge preparation involved adding appropriate amounts of various metal nitrate salts to sodium nitrate/nitrite solutions that was acidified with nitric acid to prevent formation of precipitates. Then, radionuclide surrogates (see below) were added to the solution. The final step in sludge

preparation involved making the mixes highly caustic with NaOH and taking splits for aging at room temperature, 60°, and 90° C. Higher temperatures were used to accelerate aging and to mimic the fact that some wastes experienced in-tank temperatures near their boiling points for prolonged periods. At various times subsamples of these different aged sludges were washed free of the fluid and analyzed by X-ray diffraction as well as TEM. Chemical analyses of the coexisting fluids and solids were obtained using either DCP-ES (early tests) or later on ICP-MS.

Table 1 - Molar concentrations of significant sludge components in artificial acid wastes.

	BiPO4	TBP – U recovery	REDOX	PUREX	PUREX	NCAW -late PUREX
	Al Cladding	Al Cladding	Al>>Zr Clad	Al Cladding	Zr Cladding	Al/Zr Clad
Al	8E-2	0	1.1	8E-1	0	6E-1
Fe	3E-2	5E-2	5E-2	1E-1	4E-2	1E-1
Al/Fe	2.6	0	22	6.7	0	0
Cr	3E-3	3E-3	7E-2	8E-3	3E-3	2E-2
Ni	2E-3	2E-3	4E-3	1E-2	1E-3	6E-2
Zr	3E-4	0	0	0	1E-1	4E-3
Bi	1E-2	0	0	0	0	0
Ca	2E-2	2E-2	0	6E-2	2E-2	0
Si	6E-2	4E-3	4E-2	5E-2	0	8E-3
F	2E-1	0	0	0	8E-1	1E-1
P	2E-2	1E-1	0	2E-2	0	0
Pb	4E-4	1E-4	1E-2	1E-3	0	0
Mn	7E-3	0	0	3E-2	0	0
SO ₄ ⁼	5E-2	2E-1	2E-2	2E-2	2E-2	1E-1
Cd	1E-5	8E-6	0	1E-3	1E-3	0

The choice of radionuclide surrogates merits some discussion. The immediate hazard presented by HLW fluids arises from short-lived radioisotopes such as ¹⁵⁴Eu, ¹⁴⁴Ce, ¹³⁷Cs, ¹⁰⁶Ru, ⁹⁰Sr and ⁶⁰Co. The release of these radioisotopes from a leaking tank may be of considerable importance with regard to tracking short-term plume migration as well as understanding the surface exchange characteristics of various sludge and soil components. However, they do not present a long-term a hazard to the environment since they will probably decay before a decommissioned tank is breached and would not last long enough to travel far in most slow-moving ground water systems.

Instead, low activity-long lived radioisotopes are typically identified by performance assessments as presenting the greatest hazard. As outlined above, these are relatively few in number: ⁹⁹Tc > ⁶³Ni > ⁹³Zr > ⁹⁴Nb > ¹²⁶Sn > ⁷⁹Se, ¹³⁵Cs > ¹⁵¹Sm >> ¹²⁹I. Except for ⁹⁹Tc, all of these elements have non-radioactive isotopes that can be substituted for radioisotopes in order to study their affinity for artificial sludges. It is also fortunate that in oxidizing environments ReO₄⁻ is a reasonable substitute for TcO₄⁻. Actinides are more problematic. Uranium (depleted) and thorium can be handled without specialized hot cell facilities but a prohibitive administrative burden still exists even though their heavy metal toxicity greatly outweighs any danger posed by radioactivity. Still, considerable insight into the behavior of Pu might eventually be gained using a combination of U(VI) and Th(IV). The pentavalent actinides [(Pu(V) and Np(V)] may be important in a number of environments but no good nonradioactive analogues exists. However, americium and curium (both dominantly +3 valence) have good non-radioactive surrogates in the rare earth elements.

Finally, HLW fluids may contain a number of non-radioactive metals that are of concern for their chemical toxicity – notably Pb, Cd, and Cr. In all, the list of “surrogates” included Pb, Cd, Cs, Ba (for Ra), Sr, Nd (for Am, Sm, and Cm), CrO₄⁼, Se, ReO₄⁻ (for TcO₄⁻) and Co. Ni and Zn are integral parts of some synthetic sludge recipes and so are not included in the list of surrogates. Nb and Sn were not included because their extreme low solubility in neutral solutions (7) allows one to a priori predict they will not be mobilized into the groundwater. In general, depending on the experiment, these surrogates were added so that the artificial sludge solutions would contain 20 to 100 ppm prior to precipitating the sludges. These concentrations are higher than they would occur in actual wastes but this was necessary so that they would be detectable in various post-test analyses.

II Sludge Phase Chemistry

The first issue needing resolution is the degree to which the major phase chemistry of the artificial sludges resembles that found in actual tanks. Only limited data is available on actual tank contents (8,9) and not all of it refers to phases that would survive tank cleaning procedures and remain in the sludge. Further, most of this data has been gained by transmission electron microscopy which tends to bias the study toward recognizable relatively well crystallized materials that may, in fact, only be present in minor amounts. Still the tabulation of phases observed from the tanks is a useful reference point from which to judge success in fabricating artificial sludges. This list includes:

1. The principal Al-bearing phases likely to survive waste retrieval activities are boehmite (typical of high temperature sludges) and gibbsite (lower temperature sludges).
2. Amorphous and crystalline aluminosilicates are also found at Hanford, particularly where diatomaceous earth was added to retard leakage. At Savannah River these same materials make up a significant amount of the heel in the tank bottoms (9) since zeolites (used in Cs recovery) and glass frit (used in formulating waste glasses went to some tanks and subsequently altered to natrodavyne (a member of the cancrinite-family of zeolites).
3. Iron occurs principally as amorphous iron hydroxide
4. Bi occurs as a discrete Bi_2O_3 , as BiPO_4 , and as an iron bismuth silicate hydroxide that yields weak electron diffraction patterns and hence is more crystalline than the amorphous iron oxide.
5. Cr is found associated with the both Al and Fe oxide – hydroxide components.
6. Ca and P occur as hydroxyapatite.
7. Other minor phases include Bi-chromate, Fe-Bi-phosphates, amorphous discrete $\text{Cr}(\text{OH})_3$, Fe-Mn oxides, La-phosphate, $(\text{Fe,Mn})(\text{MnO}_4)_2$ and, of course, the occasional U or Pu containing oxide.

X-ray diffraction traces of synthetic sludges (Fig. 1) typically have a complex structure with sharp diffraction peaks for the few well crystallized components superimposed on a single broad hump characteristic of the amorphous (largely Fe) components in the sludge. The sludges were also characterized by transmission electron microscopy (TEM) supplemented by energy dispersive analysis and selected area electron diffraction. This examination revealed the presence of a number of minor phases as well as indicated how minor components in the sludges partitioned among the major sludge phases (Table 2).

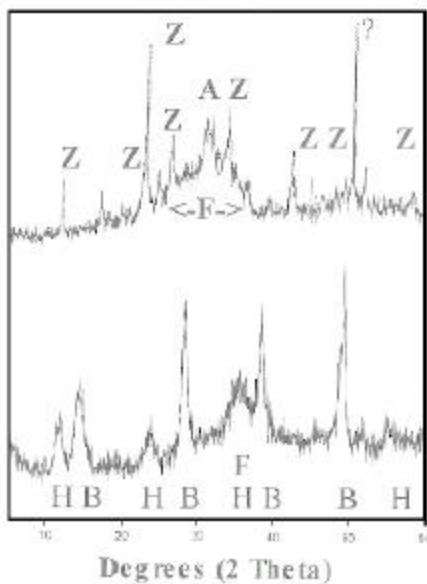


Fig. 1 X-ray diffraction patterns of synthetic BiPO_4 (top) and NCAW-PUREX (bottom) sludges aged at 90°C . B = boehmite, H = a Ni-hydroxalite resembling green rust in structure, F = ferrihydrite, Z = a cancrinite group zeolite, A = apatite.

Of greatest interest are whether the main iron and aluminum containing phases in the sludge resemble those in the actual sludges. Figures 2 and 3 present comparisons of the hydrous iron oxides found in real and artificial sludges. In both cases the morphologies of the artificial sludge particles are a good match for the real thing. However, in the case of the Bi-rich sludge electron diffraction shows that the actual tank sludge is poorly crystalline while the artificial material is still completely amorphous. The lack of crystallinity in the iron oxide phase of heated-aged sludges is of particular interest since in other systems ferrihydrite often alters to goethite (or other crystalline phases) in a matter of days (10). However, Al in particular has been noted to retard the crystallization of such materials. Entries in Table 2 for $\text{FeOOH}(x\text{l?})$ show that even if Al is absent enough other elements are incorporated into the ferrihydrite to retard its inversion to more crystalline phases.

The correspondence with the Al-bearing compounds is more complex. Both real and artificial sludges are rich in boehmite [$\text{AlO}(\text{OH})$] but the morphologies may be significantly different (Fig. 4). In addition to fine grained materials found in both real and artificial sludges the tanks also contain coarse well crystallized boehmite. It is likely that this reflects the longer aging in the real sludges, and, unlike the experiments, the supernate solutions in the tanks often underwent extreme evaporative concentration and achieved very high ionic strengths. A consequence of this difference is that artificial sludges might have somewhat greater exchange capacities than the real sludges. Zeolites are the other Al-containing phase that are occasionally abundant in sludges. To the degree that comparisons are possible, it appears that the real and artificial materials have similar morphologies (Fig. 5) and the same can be said for apatite (Fig. 6).

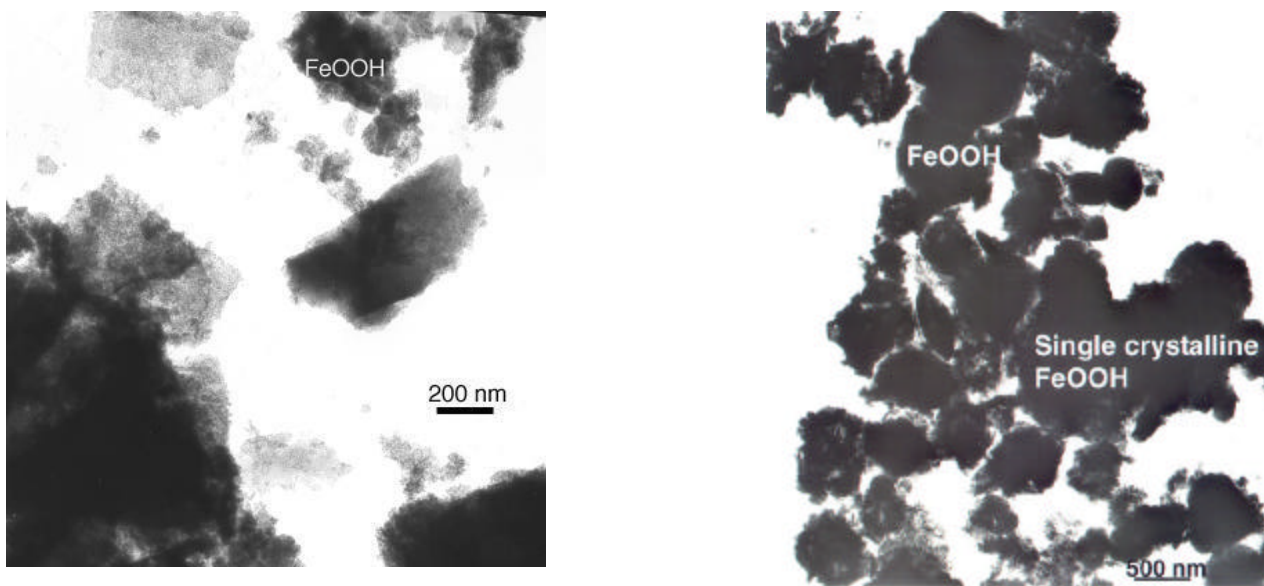


Fig. 2. Comparison of hydrous iron oxides from synthetic sludges aged at 90° C for 169 days and actual sludge from tank C-107.

Table 2 - Phases identified in artificial sludges

Data	Waste Stream	X-ray detected phases	TEM detected phases with elements by EDS
23° C 169 Days	BiPO ₄ process (1C/CW)	Apatite 2-line Ferrihydrite	Apatite Ca>Si>P>Al,Fe>Bi Bi-Fe-oxide Fe,Ca,Si>Bi>P>Al>>Mn>Cr Zeolite Si>Al>Ca>Na>>Fe>Cd
90° C 169 Days	BiPO ₄ process (1C/CW)	Apatite Zeolite	Apatite Ca>P>>Na>Bi>Pb, Trace Mn,Fe Zeolite Al, Si>>Na, Bi, Ca, Fe>Mn, P, > Cr, Trace Cr, Ni, Pb Bi metal Bi>>Na, Trace P Fe-Bi oxide Fe,Bi>>Mn,Si, >Al, P, Ca, Na, Trace Pb CaSO ₄ Ca, S>>Na ZrO ₂ , Zr>>Na Goethite, Fe>>Na Hematite, Fe>>Na
23° C 169 Days	Tributyl- Phosphate - U recovery	Apatite 2-line Ferrihydrite	Apatite, Ca,P>>Fe>>Pb, Cr, Na FeOOH (xl?) Fe>>Al, Si, P, Pb, Ca,Cr
90° C 169 Days	Tributyl- Phosphate - U recovery	Apatite 2-line Ferrihydrite	FeOOH(xl?), Fe>>Ca>Si>Ni, Pb apatite, Ca, P > Fe, Na PbO Pb>>Fe>Ca
23° C 169 Days	REDOX	Boehmite, Gibbsite Hematite (trace)	Boehmite, Al>Si>Cr, Fe >Ca Gibbsite, Na>>Al (Fe,Cr,Al,Si)OOH(xl?) Al>Fe,Cr>Si>Ca, Trace Pb, Ni Portlandite Ca>>Na Hematite Fe>>Si, Ca>Pb, Na>Ni
90° C 169 Days	REDOX	Zeolite, Boehmite, Hematite(trace), Goethite(trace)	Zeolite, Al>Si>>Ca, Fe, Si>>Cr boehmite, Al>>Si, Fe, Cr> Ca>Na> FeOOH(xl?) Al,Fe>Cr>Na, Pb, Si, P> Ti>Ni
90° C 169 Days	PUREX – Al Cladding	Boehmite, Zeolite, Hematite	Boehmite No EDS taken Zeolite (good xl) Al>Si>Na>>Fe, Ca Apatite, No EDS tanken FeOOH(xl?) Fe>>Al>Bi>Mn
23° C 169 Days	PUREX – Zr Cladding	Na ₃ ZrF ₇ , NaFe ₃ (SO ₄) ₂ NaNO ₃ Ca ₅ (SiO ₄) ₂ (OH,F) ₂	Fluorite, Ca, F>> Na, Zr, Fe >Cr, Si NaFeO ₂ Fe, Na>>Zr, Ca, Cr, Ni Na ₂ FeF ₆ Na, F, Fe>Ca>Cr,,Zr Na ₃ ZrF ₇ Na, Zr, F >>>Ca, Cr, Fe, Si
90° C 169 Days	PUREX – Zr Cladding	Mostly Unknown, 2-line Ferrihydrite	Fluorite, Ca, F, Trace Na, P, Pb FeOOH (xl??) Fe > Ca, F, P, Si, Al, Na>Pb, Ni, Zn, Cs ZrO ₂ Zr>>Ca, Fe, Si, Na > Pb
90° C 266 Days	NCAW: generic late stage PUREX	Boehmite Fe-Ni-Hydrotalcite	Boehmite Al>>Fe>>Ni>Cr,Ca, P, Ti Fe-Ni-hydrotalcite Al>Ni>Fe>>Cr, Ti, Ca Portlandite, Ca

Artificial sludge containing dense agglomerates of Fe,Si, Bi has similar morphology to real tank waste (inset).

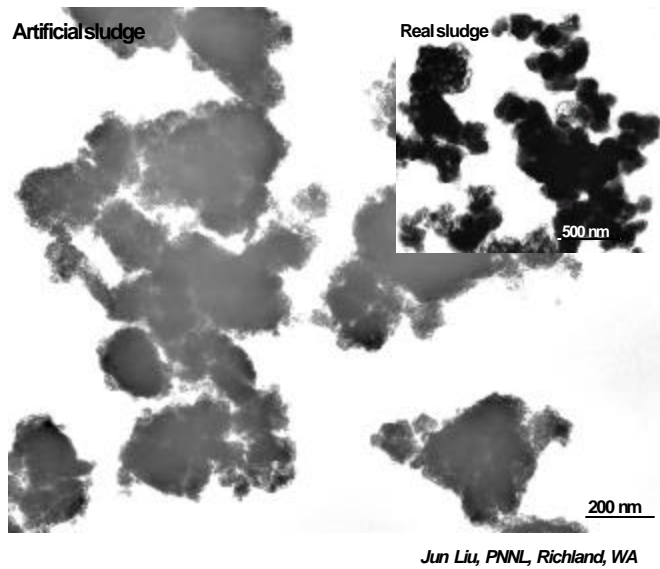


Fig. 3 Comparison of hydrous iron oxides rich in Bi and Si in artificial sludges and actual tank sludge (inset)

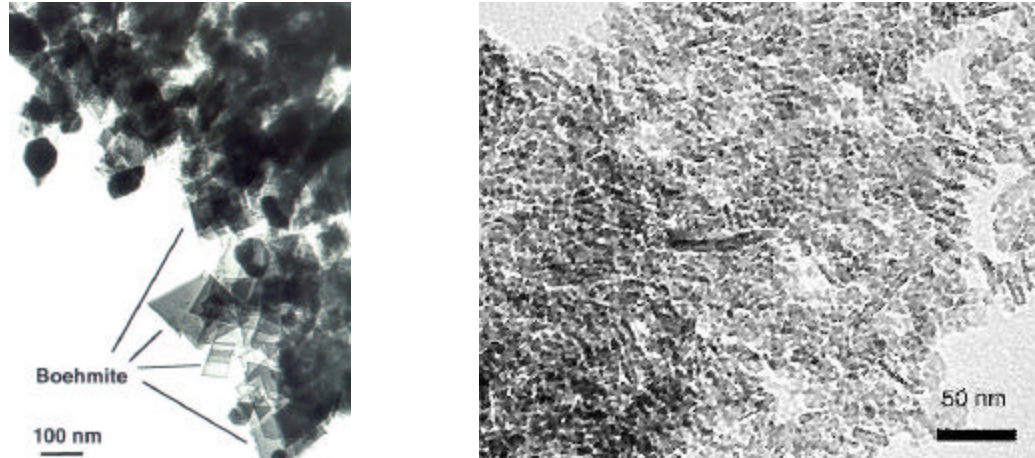


Fig. 4 Comparison of boehmite formed in tanks (left) and artificial sludges (right)

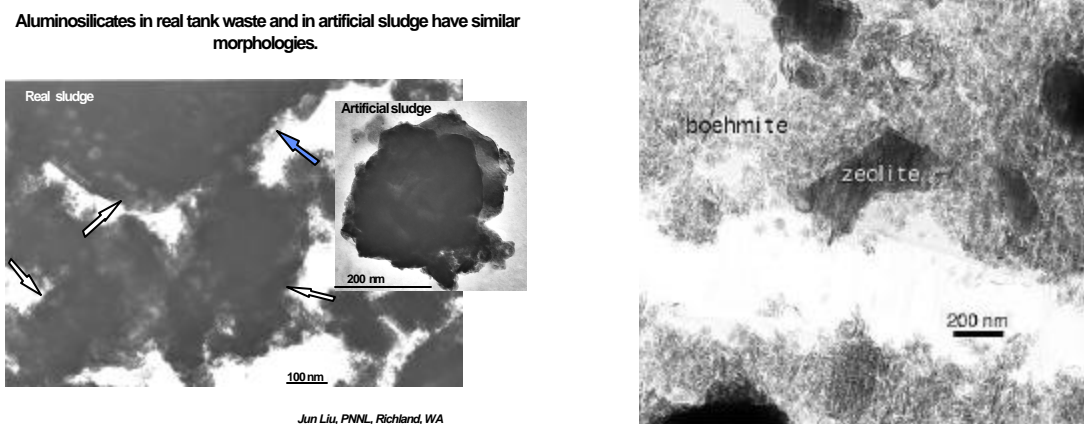


Fig. 5 Comparison of zeolitic materials from tanks and artificial sludge (left, inset). Artificial sludges may also contain coarsely crystalline zeolitic materials along with fine-grained boehmite (right)

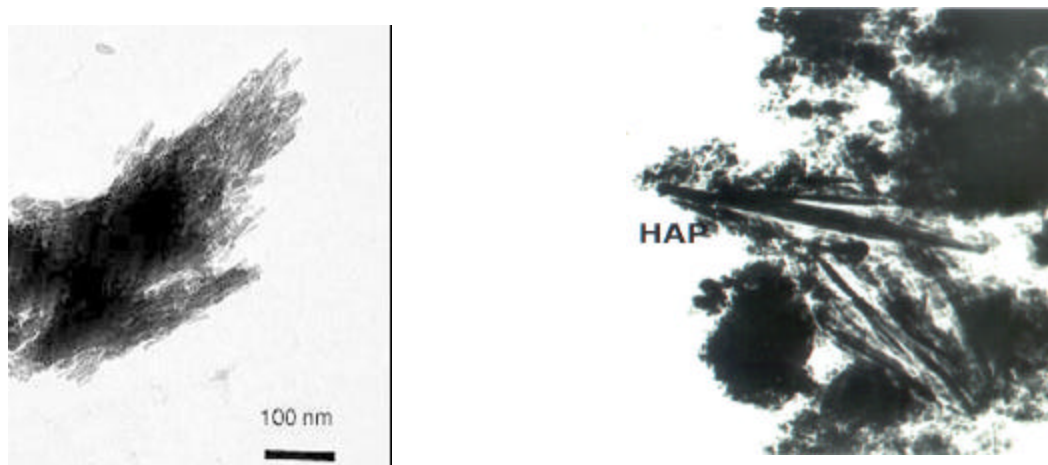


Fig. 6 Clumps of apatite crystals from artificial sludge (left) and actual sludge from Tank BY-108 (right).

III Primary Sludge-Supernate Interactions

The central issue in developing defensible tank closure strategies is how well sludges retain trace amounts of various radionuclides (or in this study their surrogates). The question is complex as the geochemical environment in a tank will change with the passage of time. The initial release will be dominated by the flushing of pore fluids in the sludges. Understanding this process depends on having a model for the partitioning of radionuclides during the initial sludge precipitation process. Once the supernate is flushed from the pores the ionic strength and pH of the pore fluids will drop significantly, though modestly basic conditions may be anticipated for a long time, particularly if a Portland cement based grout is used to fill the tanks. Eventually, though, if precipitation is high and dense vegetation covers a site groundwaters may even be slightly acidic. Such results are immediately applicable to the Savannah River setting where normal groundwaters have less than 100 ppm total dissolved solids and pH values range between 5 and 7 (11). To apply such results to Hanford would, however, require a return of the ice age conditions.

Two sets of experiments were carried out to judge the impact of sludge precipitation on the composition of the coexisting supernate. The objective of these experiments was to assess which elements were initially partitioned into the solids (and would be available for later release from sludges). The basic sludge recipes enumerated in Table 1 were employed and doped with surrogates as described above. The day after the sludges were precipitated, and prior to any heating, the supernates were filtered and analyzed by direct current plasma (DCP) emission spectroscopy. Accounting for dilution, this provided surrogate detection limits in the low ppm range. This was sufficiently sensitivity to confirm that those surrogates expected to be insoluble in strong base (7) were quantitatively removed from the liquid supernate. Rather surprisingly, small but detectable, decreases were also observed in elements existing as anions (ReO_4^- and SeO_4^{2-}) that neither sorbed or formed insoluble compounds. Further, these losses were only observed in the high aluminum REDOX and Al-PUREX sludges. Later an opportunity arose to depart from the normal research approach and confirm these findings with TcO_4^- rather than ReO_4^- (Table 3). As with ReO_4^- , the Al-rich sludges also sorbed TcO_4^- , though unlike ReO_4^- more than half of the TcO_4^- was released by heating the sludge to 90° C overnight.

Table 3 - Decreases in anionic components during preparation of artificial sludges

Sludge Type	Re	Tc	Se
Al-PUREX	40 to 29 ppm	1 to 0.6 ppm	40 to 26 ppm
REDOX	40 to 27 ppm	1 to 0.8 ppm	40 to 31 ppm

More detailed studies investigating ReO_4^- sorption onto boehmite in low ionic strength solutions were initiated (Fig. 7) and identified the mechanism responsible for removing anionic components during sludge precipitation (Table 3). ReO_4^- sorption is not significant above pH 9, and certainly would not occur in the pH 11-12 solutions in contact with the artificial sludges. However, most of the boehmite in the artificial sludges would have precipitated between pH 3 and pH 8. In this interval ReO_4^- (and other anions) would have sorbed on the freshly forming surfaces and then become occluded by further growth of the boehmite crystals. Anions sorbed in this manner would not be available to desorb at the higher pH of the final sludge solutions, thus resulting in the effects noted in Table 3. However, Ostwald ripening may cause boehmite grains to grow and recrystallize, thus releasing the anions in a high pH environment. This could account for the Tc release noted in the heated artificial sludges. Apparently SeO_4^{2-} and ReO_4^- are more strongly held since they were not released like the Tc.

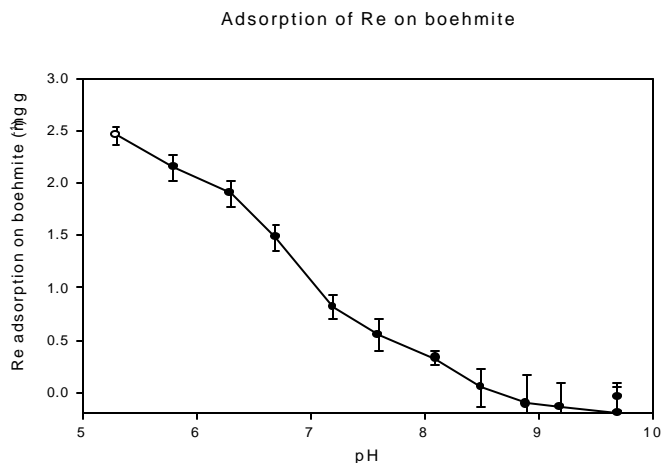


Fig. 7 ReO_4^- Kd values for sorption onto boehmite as a function of pH in 0.0005 M NaNO_3 solutions

These experiments only lasted two days and there was a suggestion that short-term recrystallization might impact surrogate retention. Thus, longer two week experiments were carried out at room temperature and 90° C, and this time the supernate fluids were analyzed by ICPMS. To do this artificial sludge solutions were doped with 80-90 ppm of the various surrogates prior to being brought to a highly basic condition. The mixtures were then split into equal parts and aged for two weeks at 25° and 90° C. At the end of this time splits of the sludge – supernate slurry were taken. One portion was filtered through a 0.2 micron filter and then the fluid was analyzed (Table 4).

Several trends are evident in this data. In many cases chromate is much higher than the level that was initially added as a surrogate. Cd, Nd, Pb, and Co were almost completely removed. Ba and Sr also showed significant removal but not to the extent of the others. Finally Cr was not strongly sorbed and in many cases the exposure to the nitrate solution oxidized the Cr⁺³ added to the sludge mix. The impact of heating samples was not large, except that oxidation of trivalent Cr was increased with temperature. Only Sr (but not Ba) showed a preference for sorption onto Al rich sludges (REDOX and Al-PUREX) over those richer in iron. Removal was not related to the Fe:Al ratio for the other surrogates.

The most interesting result was that certain of the elements typically regarded as remaining completely dissolved (e.g Cs, Se, and Re [for Tc]) were partially incorporated into the solids. However, this time there is not a clear correlation between Al content and anion (ReO₄⁻ SeO₄⁻) sorption suggests that in these experiments the ubiquitous hydrous iron oxides dominated sorption-desorption process. The shift in behavior can be understood in light of the fact that the surface properties of both Fe and Al oxides are quite variable. Depending on the particular oxide species the zero point of charge (e.g. the pH below which the surface is positively charged and hence sorbs anions) for Al oxides and hydroxides ranges from pH 9 to pH 5 while for Fe oxides and hydroxides the range is pH 8.5 to pH 6.7 (12). Thus, the characteristics of the oxides that happen to form, or evolve, in a particular experiment will determine which (if any) hydrous oxide plays a dominant role in anion sorption.

Table – 4 Analysis of post-precipitation fluids after sludges were aged for two weeks (PPM)

Element	BiPO4	TBP	REDOX	PUREX-Al	PUREX-Zr
Al/Fe-molar #	1.1	0	15.7	12.2	0
25° C Expts.					
Initial Conc. All Elements	87 ppm	85 ppm	84 ppm	79 ppm	88 ppm
Cr	77	73	108*	9.9	79
Co	<0.40	<0.40	<0.30	<0.30	<0.20
Sr	0.74	1.050	<0.20	<0.20	0.22
Cd	<0.40	<0.40	<0.20	<0.20	<0.20
Ba	7.94	4.67	6.04	4.36	5.69
Nd	<0.40	<0.40	<0.20	<0.20	<0.20
Pb	<0.30	0.57	0.65	<0.20	1.18
Se	73 (-16%)	65 (-15%)	66 (-21%)	53 (-33%)	71 (-19%)
Re	81 (-6.8%)	70 (-16%)	71 (-16%)	67 (-15%)	74 (-16%)
Cs	75 (-14%)	67 (-15%)	97 *	72 (-8.9%)	79 (-10%)
90° C					
Al/Fe-molar #	2.0	0	9.1	2.9	0
Cr	179*	141*	691*	157*	163*
Co	0.63	<0.40	<0.40	<0.30	<0.30
Sr	0.88	0.86	<0.40	<0.20	<0.20
Cd	<0.40	<0.40	<0.40	<0.20	<0.20
Ba	8.2	3.2	7.1	5.5	<0.20
Nd	<0.40	<0.40	<0.40	<0.20	<0.20
Pb	<0.30	0.80	1.8	<0.20	<0.20
Se	72 (-17%)	64 (-25%)	65 (-23%)	58 (-27%)	72 (-18%)
Re	83 (-4.6%)	72 (-15%)	77 (-8.4%)	69 (-13%)	80 (-9.1%)
Cs	82 (-5.7%)	77 (-9.4%)	75 (-11%)	72 (-8.9%)	89*

* Concentrations exceed amount added initially

Based on sludge analyses, not as -mixed proportions

IV Impacts of Decreasing Ionic Strength and pH

A second portion of the aged sludge-supernate slurry was placed in a dialysis bag and the rinse water was changed four times over a 12 day interval. This procedure was used in preference to filtration because of the colloidal nature of the sludge. Large amounts of material are lost if normal analytic filters or used, or the system clogs immediately if submicron filters are employed. Either way, it proved impossible to rinse and collect several hundred milligram batches of sludge. Roughly, the relative weights of sludge in these experiments were (BiPO₄ : TBP : REDOX : Al-PUREX : Zr-PUREX) 2 : 1 : 14 : 27 : 1 at 25° C and 2 : 1 : 9 : 8 : 1 at 90° C. Nitrate concentrations in the last dialysis rinse were less than 5 ppm and the pH had fallen to between 8 and 10. The dialysis waters were changed four times and the forth rinse fluid was analyzed for surrogates. These analyses are, thus a first assessment of what might be exist in solution once a flow after groundwater had gained some access to the sludge for some time.

Analysis of the last dialysis fluid (Table IV) revealed a trend reflecting the order of surrogate removal during sludge preparation. Releases of Re, Cs, Se and CrO₄⁻ were relatively large while Ba and Sr releases were not as pronounced but still greater than that the other surrogates. In both unheated and heated samples the Al-free TBP and Zr-PUREX sludges released relatively large amounts of Sr and Ba. But, at least at room temperature, only a small amount of Al (e.g the BiPO₄sludge) was needed to decrease these releases. The two high Al sludges (REDOX AND PUREX-AL) released relatively large amounts of CrO₄⁻, Se, Re and Cs. Heating generally seems to have enhanced slightly the release of strongly sorbed surrogates and greatly enhanced releases of Sr and Ba from the PUREX-Zr sludge while decreasing that of chromate.

Table 5 – Concentrations (ppb) in the last dialysis wash

Element	BiPO4	TBP	REDOX	PUREX-Al	PUREX-Zr
25° C					
Al/Fe-molar	1.1	0	15.7	12.2	0
Cr	3.2	0.8	46.5	128	2
Co	>0.4	>0.4	>0.4	>0.4	>0.4
Sr	0.8	100	1.3	0.6	208
Cd	>0.4	>0.4	>0.4	>0.4	>0.4
Ba	0.7	34.6	1.3	0.8	18.7
Nd	>0.4	>0.4	>0.4	>0.4	>0.4
Pb	>0.3	>0.3	>0.3	>0.3	>0.3
Se	>4.5	>4.5	8.9	8.0	>4.5
Re	>0.2	>0.2	2.1	0.6	>0.2
Cs	11.6	1.4	132	14.3	0.3
pH	8.9	7.3	10.2	9.8	8.4
90° C					
Al/Fe-molar	2.0	0	9.1	2.9	0
Cr	7.6	1.8	38.4	75.5	3.9
Co	0.3	1.5	>0.2	0.4	>0.2
Sr	0.8	4.9	36.4	0.5	760
Cd	>0.3	3.1	>0.3	>0.4	>0.3
Ba	0.4	2.1	1.6	0.3	92
Nd	0.4	7.4	>0.2	0.4	<0.2
Pb	0.2	1.7	>0.2	0.4	>0.2
Se	>4.5	>4.5	5.7	39.4	>4.5
Re	2.2	0.2	2.8	12.9	1.0
Cs	13.9	7.5	24.9	26.3	1.9
pH	9.6	8.4	10.0	10.0	7.6

The sludges were then rinsed from the dialysis bags, suspended in deionized water, and the pH was then lowered to the 5-7 range with nitric acid. After aging for a week the fluids filtered through a 0.2 micron filter and analyzed (Table 6). Predictably, this process greatly enhancing releases of most surrogates. Apparent exceptions are chromate, Se and Re, which were probably removed by the earlier dialysis treatment. Notable are the high concentrations of elements Co, Sr, Cd and Ba relative to Pb and Nd. Nd forms insoluble hydroxides and phosphates so its release may be solubility limited while Pb retention probably is a reflection of its considerable affinity for ferric hydroxide relative to Co, Sr, Cd and Ba. The behavior of Nd, Pb, Co (in the heated sample) and Cd in the heated n REDOX vs PUREX-Al sludges is anomalous and as yet unexplained. Both mixes are rich in Al but only the REDOX mix released significant concentrations of surrogates while the PUREX-Al mix did not.

Table 6 - Trace elements leached from acidified sludges (PPB)

Element	BiPO4	TBP	REDOX	PUREX-Al	PUREX-Zr
25° C					
Al/Fe-molar	1.1	0	15.7	12.2	0
Cr	3.8	1.6	1030	7.6	>0.3
Co	36.7	567	324	101	256
Sr	1590	2310	2920	2630	704
Cd	65.9	254	488	151	97.7
Ba	767	1080	2250	1560	582
Nd	>0.4	>0.4	42.4	>0.4	>0.4
Pb	<0.3	<0.3	29.8	<0.3	<0.3
Se	>4.5	>4.5	>4.5	>4.5	>4.5
Re	>0.2	>0.2	>0.2	>0.2	>0.2
Cs	204	0.4	137	51.9	0.7
pH	5.9	5.7	5.6	5.6	5.7
90° C					
Al/Fe-molar	2.0	0	9.1	2.9	0
Cr	0.6	0.7	15.6	16.3	>0.3
Co	<0.2	496	195	0.6	76.1
Sr	257	2040	1500	1030	1220
Cd	6.4	908	729	3.1	201
Ba	121	1290	1070	52.8	601
Nd	>0.4	>0.4	1220	>0.4	0.9
Pb	<0.2	0.2	55.6	<0.2	<0.2
Se	>4.5	>4.5	>4.5	6.2	>4.5
Re	0.5	<0.2	<0.2	1.0	<0.2
Cs	83.3	2.7	5.5	40.0	0.3
pH	6.2	5.1	4.2	4.8	5.5

The final step was to analyze the solid sludge components that were left after the acidification process. These analyses (Table 7) are presented in two ways. For each entry the first value gives the ratio of the weight of the component being listed to the amounts of Fe+Al in the analysis times 100. In effect, this is a weight percent relative to the major metals in the sludges. A second way to view these data is to ask what the sludge analyses say about the relative retention of the different surrogates during the washing/leaching procedures described above. The basis for addressing this issue is the assumption that all of the Fe in the initial sludge recipe (Table 1) was precipitated when base was added and that none of the iron was removed later by the washing/leaching procedures. From the sludge recipes and the amounts of surrogates added it is possible to calculate "as mixed" surrogate:Fe ratios. Table III suggests that except for Cs, Se, Re, and Cr the remainder of the surrogates were removed quantitatively. Where the basic sludge recipe contained Pb, Cr or Cd (Table I) in addition to what was added as a surrogate this amount was also added in computing values for the "as mixed" starting ratio. "As measured" surrogate: Fe ratios were also calculated from analyses of the sludges solids. The final step was to divide the "as measured" ratio by the "as mixed" to give an assessment of the relative enrichment or depletion of each surrogate in all

five mixes. For surrogates that were quantitatively removed during neutralization (Table 4) values greater than one indicates enrichment, while a value below 1 implies that a surrogate has been lost during the washing/leaching process. For Cs, Se, Re the value that discriminates between enrichment and loss during washing/leaching is the fraction sorbed (Table 3) rather than 1.

Table 7 – Surrogate concentrations (x 100) relative to Fe+Al, and measured surrogate : Fe vs. “as mixed” surrogate : Fe ratios ()

Element	BiPO4	TBP	REDOX	PUREX-Al	PUREX-Zr
25° C					
Al/Fe-molar	1.1	0	15.7	12.2	0
Ba	6.00 (1.62)	11.7 (3.00)	0.12 (0.29)	0.67 (0.71)	3.01 (0.67)
Cd	0.45 (0.12)	12.9 (3.31)	0.27 (0.65)	1.99 (0.90)	6.81 (1.08)
Co	0.37 (0.10)	5.54 (1.42)	0.38 (0.96)	1.66 (1.76)	4.92 (1.10)
Cr	0.61 (0.07)	9.32 (0.89)	16.1 (1.04)	6.5 (1.33)	7.6 (0.61)
Sr	0.027 (0.07)	2.76 (0.71)	0.03 (0.06)	0.015 (0.16)	0.31 (0.07)
Nd	5.66 (1.52)	10.67 (2.74)	0.41 (0.99)	2.01 (2.14)	6.66 (1.49)
Pb	2.64 (0.74)	1.77 (1.43)	0.67 (1.10)	2.17 (1.03)	0.47 (1.49)
Re	0.003 (9E-4)	0.006 (2E-3)	0.001 (3E-3)	0.007 (8E-3)	0.014 (3E-3)
Cs	0.040 (0.01)	0.024 (0.006)	0.0007 (0.001)	0.003 (0.004)	0.028 (0.006)
90° C					
Al/Fe-molar	2.0	0	9.1	2.9	0
Ba	3.91 (1.37)	3.32 (0.85)	0.33 (0.49)	1.09 (1.74)	5.88 (1.30)
Cd	1.44 (0.97)	4.37 (1.12)	0.40 (0.61)	0.99 (1.12)	0.26 (0.41)
Co	2.36 (0.83)	3.29 (0.84)	0.50 (0.75)	0.59 (0.95)	4.92 (0.88)
Cr	0.96 (0.14)	2.9 (0.28)	11.1 (0.45)	1.6 (0.51)	4.6 (0.37)
Sr	2.81 (0.98)	0.52 (0.13)	0.05 (0.08)	0.66 (1.05)	0.90 (0.20)
Nd	2.90 (1.01)	9.29 (2.39)	0.34 (0.52)	1.24 (1.98)	5.89 (1.32)
Pb	1.87 (0.76)	0.74 (1.03)	0.31 (1.49)	0.82 (0.88)	1.8 (1.74)
Re	0.015 (5E-3)	0.014 (4E-3)	0.006 (1E-2)	0.003 (4E-3)	0.30 (7E-3)
Cs	0.31 (0.01)	0.007 (0.02)	0.003 (0.005)	0.006 (0.009)	0.017 (0.004)

Values greater than roughly 1.15 are particularly problematic and cannot be ascribed to analytic errors. Nor do they probably represent the systematic loss of iron from a sample since, in such instances, all the ratios for a particular sample would be skewed toward high values. Rather, it is likely that they represent a lack of homogeneity in the samples; a nugget effect in which a phase enriched in a particular element was preferentially incorporated into the sample. The balance of the nuggets seemly are associated with, Ba, Pb, Nd, and 25° C TBP sludges. The existence of Ba-rich nuggets, and the absence of similar Sr-rich materials, may seem problematic. However, this can be explained noting that both Table 4 and Fig. 10 suggest that hydrous iron oxides would scavenging Sr better than Ba. Thus, Ba would have been more available than Sr to participate in mineralogic reactions occurring later in the titration when hydroxyapatite formation would start. A likely suspect would be the high pH nucleation of apatite grains. The existence of clumps of apatite crystals has been verified for both artificial and actual sludges (Fig.6). This may also explain why so many of the nuggets seem to be associated with the TBP sludge. This sludge (Table 1) contains almost an order of magnitude more phosphate than the other mixes, and comparable amounts of calcium. In contrast, the REDOX waste contains no phosphate – so cannot form apatite. This mix has only one nugget, Pb, and TEM studies (Table 2) have recorded the segregation of a separate Pb-rich phase in some sludges. There are two possible explanations for the Nd nuggets. Nd hydroxide is possible, particularly for the REDOX sludge where the last low pH treatment liberated detectable Nd to the solution. However, the low pH treatment failed to liberate detectable Nd from the other sludges. This anomalous low pH stability, and the fact that exceptions to Nd nugget occurrences were associated with the REDOX sludges, both suggest that in other sludges apatite or NdPO₄ plays the dominant role in retaining Nd.

Once the nugget effect is dispensed with other trends are also apparent in the data set. A relatively large number of the samples in Table 7 show significant Sr depletion. This is consistent with the Sr being associated with the FeOOH, and it having been sorbed onto this material at a high pH relative to several other metals in the experiment (Fig. 10). In contrast Co, Pb - and presumably Cd, (which sorbs similarly

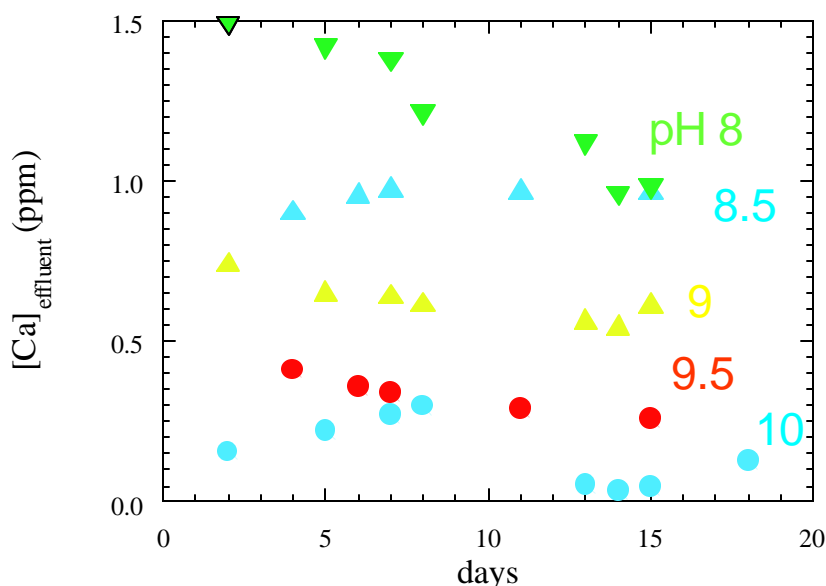
to Co (12)), would have sorbed earlier in the neutralization process (e.g. at lower pH values). Thus, they would have been occluded to a greater degree than Sr by the later growth and agglomeration of ferrihydrite particles. It follows that a larger proportion of these three early-sorbed elements would remain in the solid sludges as the ionic strength and pH decreased. Cr ratios in unheated samples are generally high and erratic while those in heated sludges are lower and more regular. This simply reflects the fact that in heated samples a significant amount of (insoluble) Cr^{+3} hydroxide was oxidized to chromate that was not strongly sorbed from the high pH solutions during the two week aging period.

The dominant feature of the Re and Cs data (along with Se, which was not detectable in the leachates so no entries appear in Table 7) is that essentially none was retained past the last step of the washing process. Fluid analyses from the last dialysis wash and the acidification step failed to detect significant Re releases. Hence, it is likely that any Re sorbed during the sludge precipitation could be released readily and left during the early dialysis washes. Cs on the other hand, appeared in significant amounts in both the last dialysis wash and the acid treatment fluids. However, this only occurred in experiments associated with Al-bearing sludges. Both the TBP and Zr-Purex sludges yielded rinse solutions that were notably deficient in Cs. Cancrinite zeolites are a ubiquitous Al-containing constituent of sludges and seem to be a logical choice as a Cs sink. However, studies directed at understanding the fate of leaked tank fluids determined that freshly precipitated hydrous Al-hydroxides are more likely to retain Cs than cancrinite zeolites (13).

Finally, the question arises regarding the importance of aging. The only instance in Table VI where there is a consistent difference between the 90° C and room temperature experiments is with the BiPO_4 sludge. For this mix heating improved the surrogate retention ability of the sludge for Cd, Co, Sr and Re. Ba and Nd were in excess of their theoretical maximum at both low and high temperatures and retention of Pb remained constant at about 75% of the theoretical maximum. The only thing significantly different about this mix is the presence of Bi, which one may speculate, may interfere with sorption sites in unheated samples.

V Hydroxyapatite Studies

The likely importance of apatite as a sink for radionuclides was recognized early in the program. Phase one activities involved synthesizing hydroxyapatite and then measuring dissolution rates using a flow-through reactor as a function of pH and ionic strength. The buildup of Ca was measured in solutions that were greatly undersaturated with respect to apatite (Fig. 8). This information was then used in conjunction with the fluid flow rate and surface area of the sample to calculate dissolution rates (Fig. 9). Initial observations also suggest that dissolution rates are almost independent of changes in ionic strength.



.Fig. 8 Ca release from hydroxyapatite as a function of pH at 25°C.

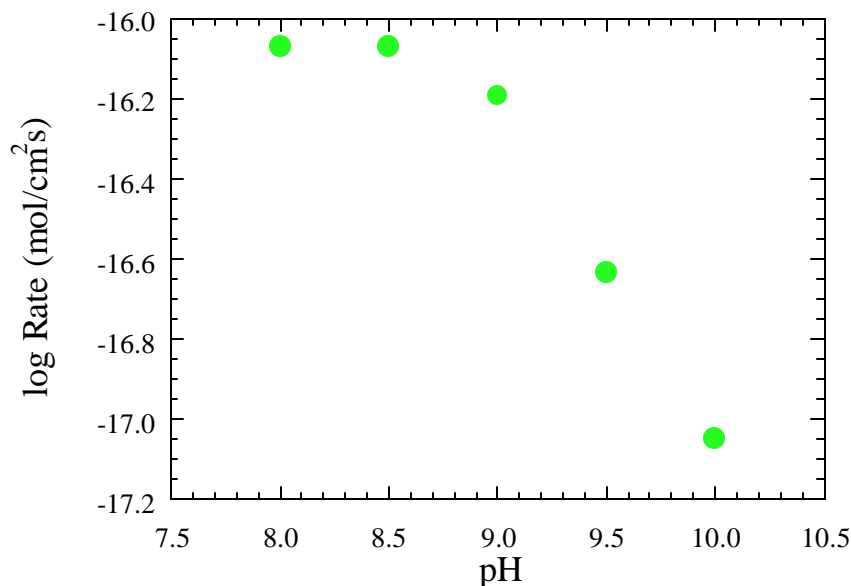


Fig. 9 Hydroxyapatite dissolution rates as a function of pH at 25°C.

VI ReO_4^- Sorption On Simple Hydrous Fe-Al Oxides (KLN, B.W. University of Colorado)

“At the University of Colorado, investigation of the aging of simplified sludge compositions is in progress. Iron and aluminum comprise the bulk of most HLW sludges at Hanford; therefore, low Al/Fe sludges are synthesized to approximate Bismuth Phosphate and PUREX wastes, whereas high Al/Fe sludges simulate REDOX waste. The behavior of rhenium as an analogue for technetium (^{99}Tc) in the aging sludges is also being monitored. Experimental samples are prepared as acidic Fe(III)-Al nitrate solutions and then “neutralized” at room temperature to pHs of 13.1-13.7. These samples are aged in a water bath at 90°C for three months. Solids and solutions are fully characterized at the ends of the experiments by X-ray diffraction, atomic force microscopy (for crystallite morphology), and specific surface area; and, by UV-Vis spectroscopy (Fe and Al), ICP-MS (Re), and pH measurement, respectively. Transformation of solids from amorphous precipitates to crystalline materials (hematite, goethite, bayerite, and gibbsite depending on initial solution composition) is complete after only 120 hours. Aging has been investigated in the presence and absence of 40 ppm Re (as perrhenate: ReO_4^-). While Re oxides are expected to be fully soluble at the pH/Eh conditions of the experimental solutions, the similarities (size, charge, stereochemistry) among the monovalent aqueous anions of Re, Al, and Fe suggest that perrhenate may interact strongly with precipitating metal-oxyhydroxides. Differences in transformation rates of the solids have been observed in both the low and high Al/Fe systems when Re is present. Also, the low Al system solids retain more Re with aging time than the high Al solids, although the concentrations are relatively small at ~ 10-100 ppb Re. Partition coefficients of Re between solid and solution are being determined as a function of aging time. Planned experiments include adding Ni and Si as solution components. The formation of a layered-double hydroxide phase is possible in the presence of Ni. Such a phase has an anionic interlayer to balance excess positive charge in the octahedral sheets. Perrhenate could reside in the interlayer, resulting in a higher solid/liquid Re partition coefficient. Silicon is known to inhibit the transformation rates of Fe oxyhydroxides, which may also contribute to higher Re partition coefficients with aging. The presence of Si could also possibly lead to the formation of a Ni-aluminosilicate clay.”

VII Geochemical Modeling

Finally, in those cases where Fe-hydrous oxides dominate, it is possible to employ theoretical geochemical models (e.g., a code named REACT) to predict the relative sorption of different components (Fig. 10). Results of this modeling clearly reflect several trends observed in Tables 4 and 5. As the pH becomes highly caustic it is predicted that Ba should, and did, remain in solution to a greater degree than Sr. However, raising the carbonate concentration above 10^{-4} molar reverses the predicted order due to the lower solubility of BaCO_3 compared to that of SrCO_3 . As the pH falls it is also predicted that more Sr than Ba should be released. Where phosphate does not interfere (e.g., the REDOX and PUREX-Zr experiments) the sludges exposed to lower pH values do contain less Sr than Ba (Table 5). Lead and Eu (for Nd) are strongly removed from solution. All of the recipes contain at least some hydrous iron oxide and Pb is predicted to strongly sorb onto this component over the entire pH range as well as form an insoluble carbonate above about a pH of 8 (Fig. 10). Thus, it is unclear why the TBP and REDOX fluids from the lab tests still have detectable Pb levels, when the others do not. These fluids do not appear to share any component in anomalous amounts that would account for this behavior (Table 1). Theoretically, Co should be relatively immobile over the entire pH range. The low Co concentrations in the synthesis fluids (Table 4) and generally high Co retention in the acid-treated sludges (Table 5) generally agrees with the model. The code also predicts that SeO_4^- would not be strongly sorbed over the upper half of the pH range examined. Thus, it is not surprising that little was removed from the synthesis fluid, and that what was scavenged was removed by subsequent washes having a neutral to mildly basic pH

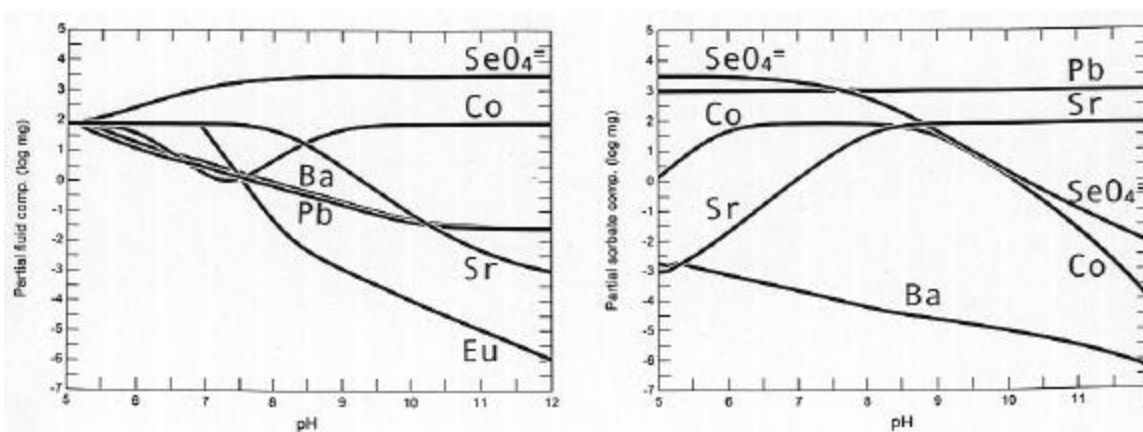


Fig. 10 Theoretical model of surrogate precipitation and sorption on hydrous iron computed using the REACT code (13). Computed based on 80 ppm Se, Co, Pb, Ba, Sr, and Eu, in a matrix solution containing 0.3 molal sodium and nitrate and 0.001 molal carbonate. 1000 grams of solution are mixed with 100 grams of freshly precipitated $\text{FeO}(\text{OH})$. Changes in dissolved components (left) reflect both sorption and precipitation reactions. The amounts of materials that are actually sorbed are presented on the right. Note: the sorption database does not evaluate Eu. Thus, all changes in Eu concentration reflect $\text{Eu}(\text{OH})_3$ precipitation and no Eu entry appears in the right hand panel.

Finally by scaling the relative amounts of fluid and hydrous iron oxide it is possible to compare the experimentally measured trends in fluid chemistry from the leached sludges with the output of the model (Fig. 11). This is procedure is somewhat artificial as the ratio Fe-oxide : solution was selected to gave the best fit at the high pH range but the results are illustrative of the possibilities this approach offers in predicting the release of radionuclides from sludges, particularly if it had proven possible to expend the database to include aluminum hydroxide. In general, it is possible to represent the quantitative changes in Ba and Sr successfully but the more complex chemical processes impacting the mobility of Co, Eu and Pb were not well represented. Selenium behavior was also modeled correctly in that both model and experiment predict that by the time low pH values are reached little should remain in solution.

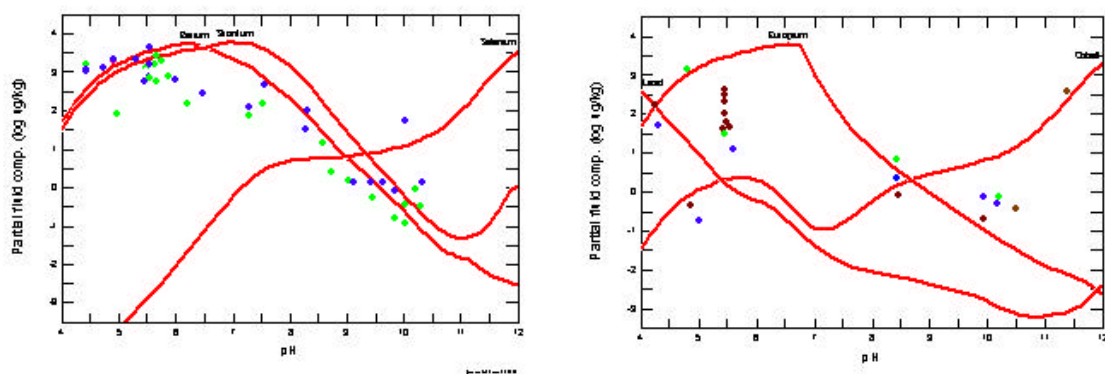


Fig. 11 Comparison of aqueous concentrations from dialysis experiments (dots) with those predicted by the REACT code (lines). Left, Se, Ba(green dots) and Sr (red dots). Right, Co(brown dots) Eu (green dots) and Pb (blue dots).

VIII AlO(OH) Compared to Hydrous Iron Oxide

Although an analogous database does not exist for hydrous aluminum oxides the behavior of some of the divalent surrogates can be assessed based on the studies in simple systems tabulated in the literature. Kinniburgh, et al.(15) reviews the sorption of a variety of divalent cations onto freshly precipitated Fe and Al hydroxide gels (Table 8). These studies were carried out at room temperature and employed a 1m NaNO₃ matrix solution. Although the order in which elements are released differs slightly for the two gels it is evident that the lowest pH values reached in the sludge leaching experiments Sr and Ba should be completely desorbed while only a portion of the Co and Cd should have been released. Pb should remain fixed in all case. Taking into account the nugget effect these trends are generally observed, though Co and Cd are more strongly retained than might be expected based on the pH of 50% release values tabulated in Table 8. One might infer that there should also be a significant difference between the behaviors of different sludges since of Al oxide gels release their cations at higher pH values than Fe oxide gels. This trend, however, is not observed in the sludge leaching data set. The likely explanation is that all the sludges contained enough Fe to dominate the sorption/desorption behavior of the samples. Support for this is particularly evident in the REDOX mixes that are free of the apatite, and hence the nugget effects resulting in elevated Ba values. Table 8 also indicates that Ba would be retained in preference to Sr on Fe oxide gel but the trend is reversed for Al-oxide gel. In the REDOX waste Ba is retained in preference to Sr even though the Al : Fe ratio is the highest value obtained in the synthetic sludge mixes.

Table 8 - Relative releases of select divalent cations sorbed on freshly precipitated Fe⁺³ and Al⁺³ gels (from Kinniburgh, et al., 15)

Release From Fe-Hydroxide	50% Release pH value	Release From Al Hydroxide #	50% Release pH value
Pb	3.1	Cu	4.8
Cu	4.4	Pb	5.2
Zn	5.4	Zn	5.6
Ni	5.6	Ni	6.3
Cd	5.8	Co	6.5
Co	6.0	Cd	6.6
Ba	*7.14	Mg	8.1
Ca	*7.30	Ca	*8.2
Sr	7.4	Sr	9.2
Mg	7.8	Ba	*9.3

* Values interpolated based on simplified system responses also reported in (#12)

Results for freshly precipitated Al-gel; aging shifts pH values for 50% release about one pH unit higher

IX Cancrinite Stability Studies

Thermodynamic analysis on the stability and solubility was conducted using available published data for CO₃ cancrinite (16,17,18,19) assuming a similar equilibria with the NO₃ counterpart. The data was regressed through a temperature range from 90 to 200°C and subsequently extrapolated to lower temperatures (Fig. 12). Activity phase diagrams were generated at pH 12 and a sodium activity of 8.9 using Si and Al values tabulated in the TWINS Tank Waste chemical database (Fig. 13). Analysis of the TWINS data along with constructed diagram shows that the data falls almost in its entirety in the stability fields of analcime and Na-clinoptilolite, rather than cancrinite. Note that in the activity phase diagrams, the TWINS data has not been speciated at any temperature and it is assumed that total Al concentration almost equals to the total Al(OH)₄⁻ concentration in the waste solution at a high pH.

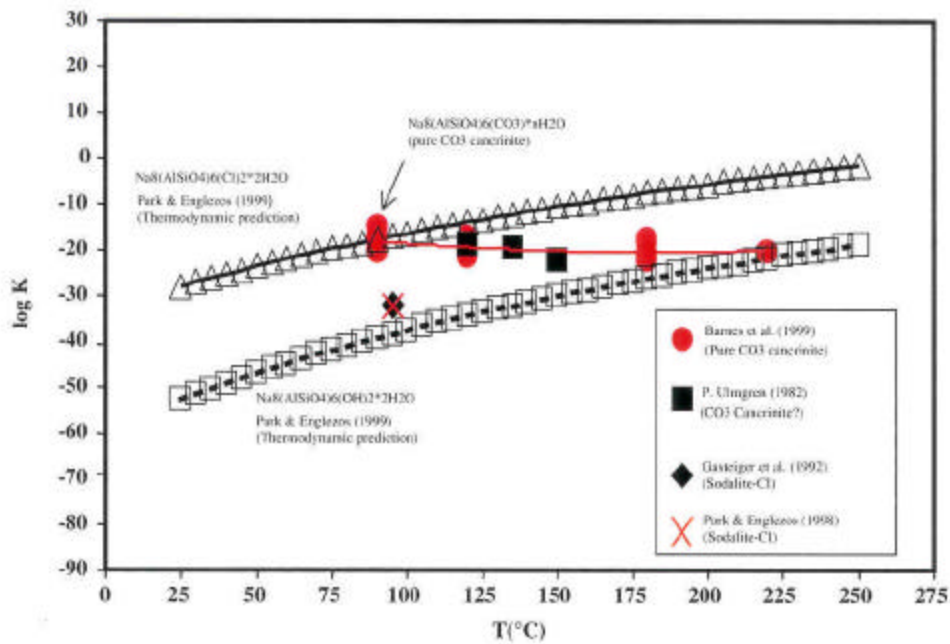
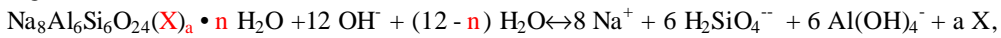


Fig. 12 The dissolution reaction for a cancrinite can be written as:



where $\text{X} = \text{Cl}^-, \text{OH}^-, \text{NO}_3^-$ or CO_3^{--} ; $a = 2$ for Cl^- and OH^- or 1 for CO_3^{--} ; n = number of H_2O molecules.

From this, it follows that if cancrinite equilibrates with a solution the following mathematical identity must be satisfied: $K_{\text{eq}} = [\text{Na}^+]^8 [\text{H}_2\text{SiO}_4^{--}]^6 [\text{Al}(\text{OH})_4^-]^6 [\text{X}]^a / [\text{OH}^-]^{12}$.

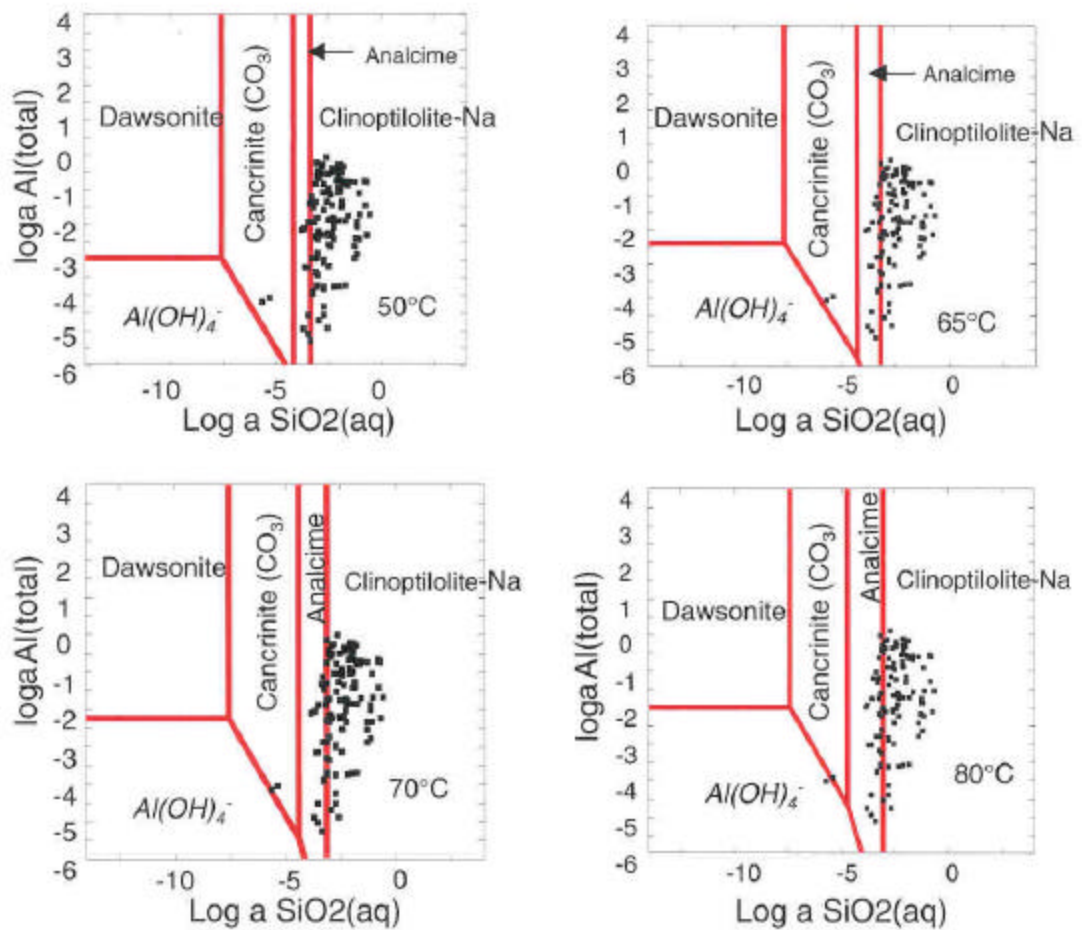


Fig 13 Activity diagrams for Hanford tank fluid compositions showing the zeolitic phases with which they are supposedly equilibrated based on the current model.

Although the modeling results are encouraging in that zeolitic phases are predicted the mineralogy is incorrect and indicating the formation of zeolites having lower Al:Si ratios than that of cancrinite. This could reflect a number of shortcomings in the present model. Proper chemical speciation of these concentrated caustic fluids requires special treatment involving Pitzer parameters that are lacking for some species relevant to this system. In this regard silica presents a particular problem – which may explain why analcime and Na-clinoptilolite are predicted though neither have been reported in the tanks waste. In addition, these results are based on data for carbonate cancrinite while a nitrate cancrinite is likely to be the phase found in the tanks.

For this reason, the solubility of NO_3 cancrinite needs to be further investigated to establish a sound thermodynamic basis of its solubility controls on caustic fluid chemistry and allowing for predictions on its stability as a function of tank temperature and fluid composition. At the time the program was terminated NO_3 -cancrinite had been successfully synthesized and analyzed with regard to both structure and composition. Comparison of the obtained XRD spectra with those catalogued for CO_3 cancrinite show some good correspondence between major peaks for both phases (Fig. 14). However, there are slight differences such as small 2-theta shifts in peak positions and intensities. Electron Microprobe Analysis (EMPA) suggest that the composition or stoichiometry of the synthesized phase closely correspond to that of $\text{Na}_8(\text{AlSiO}_4)_6(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$. Thermogravimetric analyses of the synthesized cancrinite shows that $n \sim 2$. Solubility of the NO_3 cancrinite at 25, 40, 60, 80, and 100°C and P_{sat} would have been the subject of a future study had program funding been extended.

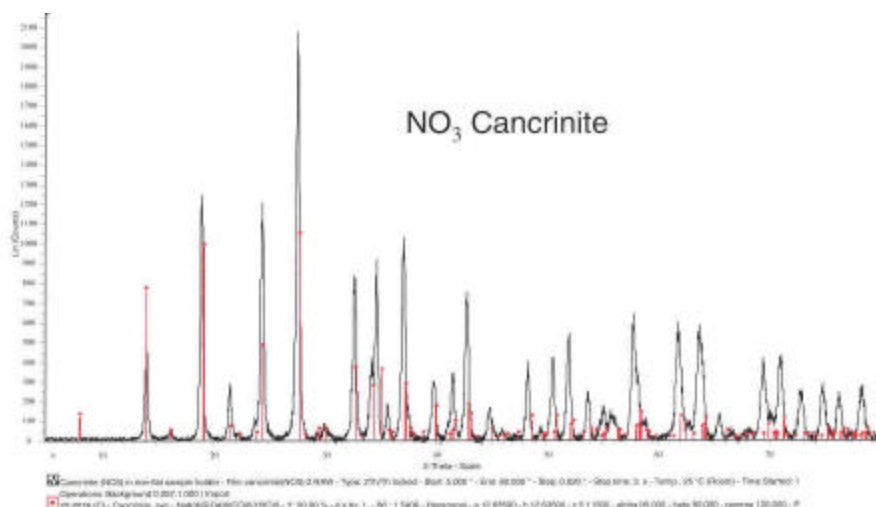


Fig. 14 X-ray diffraction pattern of synthetic NO₃-cancrinite matched with the PDF-reference pattern (red) for cancrinite.

X Conclusions

This study was undertaken to address two issues: is it possible to develop non-radioactive artificial sludges that resemble those actually found in high level nuclear waste storage tanks and, secondly, what fraction of the radioisotope inventory left in tanks would be mobilized if normal groundwater gain access to the sludge.

At least for the major sludge phases, it is apparent that one can, indeed, mimic what forms in HLW tanks. To demonstrate this it was first necessary to ferret out a considerable amount of detailed process information that was then recast to provide recipes for the main process waste streams. However, once the recipes have been worked out the procedures for synthesizing a reasonable range of artificial sludges is not particularly difficult, nor does the finished product have to age for more than a month before it can be used in testing. The one significant defect seems to be the size (but not the phase identity) of the boehmite crystals, which significantly larger in real sludges. This is unlikely to change the chemistry of sludges but could impact rheologic test results should these sludge-supernate mixes be used to research the pumping of waste slurries around the tank farms at Hanford and Savannah River.

Although much remains to be learned regarding potential sludge-groundwater interactions, the existing data clearly demonstrates that the complete radionuclide inventory of a decommissioned tank should not be regarded as mobile and, hence, a threat to the surrounding environment. Instead, it appears that a combination of modeling based on well described properties of hydrous iron oxide, solubility limits derived from thermochemical databases and some rudimentary experiments would provide reasonable guidelines in developing performance assessment source terms for a variety of tank decommissioning scenarios. These, in turn, should help significantly in choosing the safest and most cost effective tank closure options.

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