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Phase Chemistry and Radionuclide Retention from Simulated Tank Sludges

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ABSTRACT

Decommissioning high level nuclear waste tanks will leave small amounts of residual sludge clinging to the walls and floor of the structures. The permissible amount of material left in the tanks depends on the radionuclide release characteristics of the sludge. At present, no systematic process exists for assessing how much of the remaining inventory will migrate, and which radioisotopes will remain relatively fixed. Working with actual sludges is both dangerous and prohibitively expensive. Consequently, methods were developed for preparing sludge simulants and doping them with nonradioactive surrogates for several radionculides and RCRA metals of concern in actual sludges. The phase chemistry of these mixes was found to be a reasonable match for the main phases in actual sludges. Preliminary surrogate release characteristics for these sludges were assessed by lowering the ionic strength and pH of the sludges in the manner that would occur if normal groundwater gained access to a decommissioned tank. Most of the Se, Cs and Tc in the sludges will be released into the first pulse of groundwater passing through the sludge. A significant fraction of the other surrogates will be retained indefinitely by the sludges. This prolonged sequestration results from a combination coprecipitated and sorbed into or onto relatively insoluble phases such as apatite, hydrous oxides of Fe, Al, Bi and rare earth oxides and phosphates. The coprecipitated fraction cannot be released until the host phase dissolves or recrystallizes. The sorbed fraction can be released by ion exchange processes as the pore fluid chemistry changes. However, these releases can be predicted based on a knowledge of the fluid composition and the surface chemistry of the solids. In this regard, the behavior of the hydrous iron oxide component of most sludges will probably play a dominant role for many cationic radionuclides while the hydrous aluminum oxides may be more important in governing anion releases.

INTRODUCTION

Cold War reprocessing of irradiated reactor fuel produced millions of gallons of highly radioactive liquid wastes. Pending final disposal these fluids were stored in underground tanks. Although the waste was initially dissolved in nitric acid this storage method dictated that the fluids would have to be be rendered highly caustic prior to storage in the tanks. In addition, the nitrate to nitrite was adjusted to assist in passivating the mild steel tank shells (1). Raising the pH of these fluids to values in excess of 12 initiated precipitation of a variety of compounds that slowly aggregated to produce the insoluble residue known as sludge. Where tanks have remained continuously wet sludge may have the conhsistency of thick paste but where tanks boiled dry the material has solidified to form a hard "bisque". Other main categories of materials presently in the tank are salt cake (soluble salts such as NaOH, $NaNO_3$, $NaNO_2$, Na-aluminate etc.), and a residual fluid, "supernate" that is typically highly caustic as well as being rich in nitrate, nitrite, and aluminate. Some radioactive fission products such as rare earths and Sr should be strongly partitioned into the sludges, while others, such as Cs, Tc, and Se are traditionally regarded as remaining primarily in the supernate (or salt cake when the supernate has been evaporated to dryness) (2). The behavior of U, Th, Pu, Np and Am will vary depending on the supernate chemistry.

Decommissioning the tanks will involve removing most of the contents by a variety of washing processes. It will, however, prove impossible to remove all the sludge. After being filled many tanks experienced significantly elevated temperatures (3) and a few were even allowed to boil to partial dryness. Dehydration in conjunction with recrystallization processes have produced rigid "heels" adhering to some tank bottoms . Under less extreme situations the sludges have assumed the consistency of a thick paste that will not be readily dislodged. This leaves the options of either completely removing the tank once it is empty or demonstrating that radionuclide releases from the residual sludges present little long term danger to the surrounding environment. Removing the tanks would be prohibitively expensive so it is incumbent on the various stakeholders to assess what level of waste removal must be achieved in order to leave the tanks in place. This assessment hinges on predicting radionuclide releases from the sludges over a wide range of conditions. Actual tanks sludges are costly to obtain and even more expensive to experiment with. Consequently, a program was undertaken to manufacture artificial sludges that would allow for experimentation in a nonradiation environment.

Sludge research naturally breaks into two parts; developing methodologies for preparing artificial sludges and then performing release experiments on sludges that were doped with non-radioactive radionuclide surrogates. ***It is the central thesis of this study that these releases will be dominated by the major element chemistry of the sludges, and that the study of artificial non-radioactive sludges can provide most of the insights needed to predict these releases.***

ARTIFICIAL SLUDGE PREPARATION

It is likely that the phase chemistry of the sludges is determined when wastes go from being strongly acidic to strongly basic prior to being placed in the tanks. Identifying the primary sludge – forming process, however, does little to simplify the problem of sludge chemistry since a multitude of different waste streams contributed to the tank contents. At Hanford five basic waste processing technologies were used over the years (4) while at Savannah River only the PUREX process was employed. The earliest Hanford process involved dissolving irradiated fuel in nitric acid and then coprecipitating Pu with $BiPO_4$.. This created a waste stream with a mixture of processing chemicals and cladding waste that provided the basis for the first sludge chemistry that was prepared synthetically. In addition, the U and much of the fission product inventory was stored separately as "heavy metal wastes".

Solvent extraction eventually won out completely over coprecipitation as a means of recovering U and Pu from irradiated fuel rods. Early technology development in this arena involved the REDOX process that employed MEBK (methyl-ethyl butyl ketone), used Al as a salting out agent, and chromate as an oxidant. Later the PUREX process was developed which returned to TBP as an extracting agent. During the tenure of the PUREX process the fuel cladding shifted from Al alloys to Zircaloy. Thus two waste streams were defined based on cladding differences. The "heavy metal waste" were also eventually reprocessed using a tributyl phosphate (TBP) solvent extraction process. This created another fission product rich waste stream that was the basis for an additional type of artificial sludge. Finally, it should be pointed out that a significant amount of the waste did not come from processing the irradiated U pellets, but rather from the dissolved claddings that confined the U pellets in the fuel rods. At an early stage most of these Al-rich wastes were mixed in with wastes from Pu recovery operations. Later, more care was taken to avoid mixing waste streams prior to neutralization. However, considerable mixing of tank contents occurred during campaigns to recover Cs and Sr. In any case, there is much more Al in the overall waste inventory than would be inferred from the sludge compositions given in Table I. The relatively pure cladding wastes streams were not simulated for this study because they only contain a small fraction of the radioactivity.

Table I - 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
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
Al/Fe	2.6	0	22	6.7	0	0

Even when tank wastes are subdivided by processes the resulting chemistry is quite complex (5). Thus, this study focused on the waste stream from each process that carried the greatest inventory or radioactive fission products. Bulk chemistries for each of these waste streams were developed (Table I) from the literature. In the case of the BiPO$_4$ 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 (4). PUREX wastes were derived principally from Agnew (ref. 4) with supplemental data from other sources (5, 6, 7). Early parts of this study also used a simplified "NCAW" (neutralized current acid waste) mix developed by PNNL to simulate late-stage PUREX processes wastes (8). Various later process adaptations also added substantial amounts of oxalate and other organics to PUREX waste streams. Considering the impact of these additions is, however, beyond the limited scope of this investigation.

Preparation of artificial sludges involved adding appropriate amounts of various nitrate salts to sodium nitrate/nitrite solutions which had been acidified with nitric acid to insure that no precipitates formed. At this stage radionuclide surrogates were also added to the solution. The immediate hazard presented by HLW fluids arises from short – lived radioisotopes such as ^{154}Eu, ^{144}Ce, ^{137}Cs, ^{106}Ru, ^{90}Sr and ^{60}Co. The release of these radioisotopes from a sequestered tank may be of considerable importance with regard to tracking short-term plume migration as well as understanding the general surface exchange characteristics of various sludge components. However, they do not present a long-term a hazard to the environment since they will decay before groundwaters transport them any significant distance.

Instead, low activity - long lived radioisotopes are typically identified by performance assessments as presenting a the greatest hazard to the environment. These can generally be divided into fission products and actinide elements. Uranium and thorium are the only actinides that can be handled without specialized hot cell facilities, and even here there is a considerable administrative barrier to their use. However, at least americium has a good surrogate in Nd, which also serves as a surrogate for the other rare earths as well. It is also commonly found that the actinides – save Np, have sufficiently high Kd values in soils that their travel is quite restricted.

The long lived fission products are relatively few in number ^{135}Cs, ^{129}I, ^{126}Sn, ^{99}Tc and ^{79}Se. Neither ^{126}Sn or ^{135}Cs are abundant relative to the others and tin is also exceedingly insoluble in most tank farm environments. This leaves I, Se and Tc that are of genuine concern for long term migration. Most of the ^{129}I and some of the ^{135}Xe (the precursor to ^{135}Cs) probably escaped during processing. Thus, minor amounts of these radioisotopes would remain in the waste to be sequestered in the sludge. I, Se and Tc all migrate as anions and so have little affinity for the surfaces of common soil minerals. Of these Tc occurs in the greatest abundance but requires specialized hot cells for handling. Fortunately, in mildly oxidizing environments ReO_4^- is a reasonable substitute for TcO_4^-. Anecdotal accounts exist of mobile Tc that is not isolated by techniques effective at scavenging TcO_4^- and also of dried sludges from emptied tanks that contain a significant amount of the total Tc inventory of the tank. The latter implies that there are also unanticipated insoluble forms of Tc. Speculation suggests that these effects arise from a variety of causes:
(1) the existence of reduced insoluble Tc oxides or hydroxides,
(2) organic complexes of possibly reduced Tc in solution, and
(3) that Tc is fixed in the Pd-Rh-Ru-Mo-Tc alloy that segregates in spent fuel, fails to dissolve during reprocessing, and may segregate into the solid sludge or travel as colloidal particles.
Because of the ambiguity surrounding these reports this program has been restricted to considering the role of the relatively well documented TcO_4^- ion.

Finally, HLW fluids may contain a number of non-radioactive metals that are of concern from their chemical toxicity – notably Pb, Cd, and Cr. In all the list of "surrogates" included Cs, Ba (for Ra), Sr, Nd, $CrO_4^=$, Se, Re (for Tc) and Co. In general these were added so that the wastes would be in the 20 – 500 ppm level of these materials. This is, generally, far higher than they would occur in actual wastes but was necessary so that they would be detectable in various post-test analyses.

The final step in sludge preparation was precipitation of the mix by adding enough NaOH to bring the pH to 12 or greater. This process was carried out as rapidly as possible without causing the solutions to boil. Once this was accomplished splits of the slurry were taken and aged at room temperature, 60° and 90° C for periods of several weeks to many months. 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 an ICP-MS.

PHASE CHARACTERIZATION

Table II compares phases identified in the various sludge mixes after aging at both room temperature and 90° C. In terms of focusing on the main sludge components bulk chemistry dictates that the principal phases formed would be those rich in Al or Fe. These two elements exhibit distinctly different behavior. Al typically forms well crystallized compounds, mostly boehmite (AlOOH), or zeolites when sufficient silica is present. Although occasional exceptions were noted the common zeolites formed were members of the cancrinite (davine) family. This is a particular interesting zeolite as it has both exchangeable anions and cations in the channels penetrating the crystal lattice. Less commonly, other forms of Al-oxy-hydroxides are also found, but these too are well crystallized.

In contrast, iron seldom yields well crystallized phases. Instead, the presence of an amorphous to poorly crystalline material termed "ferrihydrite" is usually indicated by a broad peak on the diffraction trace and the absence of other ferric oxide phases. Various crystalline forms of ferric oxide have distinctive morphologies and these are only seen rarely in TEM images. Instead what typically is observed is irregular masses rich in iron, and a host of trace contaminants (Abbreviated FEOOH(XI?) in Table II In a relatively pure state ferrihydrite inverts to more crystalline forms of iron oxide in a matter of days. TEM studies reveal that prior to significant reordering of the material a preliminary step occurs in which dense cores develop in the largely amorphous material. Even after these prolonged periods of heating no such nucleation centers were evident the synthetic sludges and no evidence was observable that the iron containing sludge phases would increase their crystallinity with additional aging.

The explanation for this behavior probably lies in the large loading of trace components in the ferrihydrite. Al in particular has a documented role in retarding the ferrihydrite crystallization. In these situations it is likely that trace elements coprecipitated with the ferrihydrite are pervasively distributed through the interior of the precipitated mass (9). The sorptive properties of hydrous iron oxides are well studied (10) and the partitioning of other minor components onto the ferrihydrite phase is to be expected.

In the case of the $BiPO_4$ process fluids it is likely that the "Fe-Bi oxide" is just a further extension of the general ferrihydrite structure and that sorption/desoprtion processes may be similar to that of more common ferrihydrites.

Table II - Phase chemistry of aged artificial sludges.

Test 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	Tri-Butyl-Phosphate - U recovery	Apatite 2-line Ferrihydrite	Apatite, Ca,P>>Fe>>Pb, Cr, Na FeOOOH (xl?) Fe>>Al, Si, P, Pb, Ca,Cr
90° C 169 Days	Tri-Butyl-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_3ZrF_7, $NaFe_3(SO_4)_2$ $NaNO_3$ $Ca_5(SiO4)_2(OH,F)_2$	Fluorite, Ca, F>> Na, Zr, Fe >Cr, Si $NaFeO_2$ Fe, Na>>Zr , Ca, Cr, Ni Na_2FeF_6 Na, F, Fe>Ca>Cr,,Zr Na_3ZrF_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 FeOOOH (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

Apart from the major phases the minor components in the sludges seem to be developed along the lines that would be predicted from bulk chemistry. Caclium and phosphate produced apatite, Zr forms hydrous zirconium oxides or fluorides, and occasionally various other Ca salts achieve saturation when there is insufficient phosphate to consume the calcium by forming apatite. In mixes relatively high in Al and Ni (NCAW mix) a layered hydroxide similar to a hydrotalcite or a green rust structure was also noted. Thus, the major – minor element make up of most waste solutions appears to produce a relatively restricted range of phases which presumably will comprise the bulk of most sludges. Of these it appears that most of the trace element associations will be associated with the hydrous iron oxides, the hydrous Al hydroxides, and the apatite.

SLUDGE – FLUID INTERACTIONS

The central issue in developing defensible tank closure strategies is how well sludges will retain the trace amounts of various radionculides (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 if the tanks are filled with a Portland cement based concrete or grout. Finally, 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.

A preliminary experimental program has been completed that addresses all three phases of the radionuclide sequestration issue. 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 the fluid was saved for analysis without further treatment for analysis (Table III).

A second split 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 ($BiPO_4$: 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 last rinse water was also analyzed (Table IV). The sludges were then rinsed from the dialysis bags, suspended in deionized water and the pH was lowered to the 5-7 range with nitric acid and aged for a week. These fluids were also filtered and save for analysis (Table V). Finally, the solids retained on the filter were rinsed with deinonized water, and extracted for analysis using an acid wash (Table VI).

The principal behaviors evident in the sludge synthesis fluid analysis (Table III) is the fact 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. Among the remaining surrogates 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.

Table - III 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 (-26.6%)	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*
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

* Concentrations exceed amount added initially

\# Based on sludge analyses, not as-mixed proportions

Analysis of the last dialysis fluid (Table IV) revealed a trend reflecting the order of removal during sludge preparation. Releases of Re, Cs, Se and $CrO_4^=$ 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 $BiPO_4$sludge) was needed to decrease these releases. The two high Al sludges (REDOX AND PUREX-AL) released relatively large amounts of $CrO_4^=$, 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.

Further lowering the pH had the effect of greatly enhancing the release of most sludge components. Apparent exceptions are chromate, Se and Re – but a likely explanation is that these had already been removed from the sludge 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 aluminum ferric hydroxide relative to Co, Sr, Cd and Ba. One anomalous, and as yet unexplained, piece of data is the relative behavior of Nd, Pb, Co (in the heated sample) and Cd in the heated samples in REDOX vs PUREX-Al sludges. Both mixes are rich in Al but the REDOX mix releases significant concentrations of surrogates - even Nd - while the PUREX-Al mix did not.

Table IV - Concentrations in the last dialysis wash (PPB)

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

Finally, Table VI presents analysis of the solid sludges 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. In those cases 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. Secondly, "as measured" surrogate: Fe ratios were also evaluated based on the analysis at the end of the washing/leaching procedure. The final step was do divide the "as measured" ratio by the "as mixed" top give an assessment of the relative enrichment or depletion. For surrogates that were quantitatively removed during the neutralization process the a value 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 V - 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

Table VI – 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)

As anticipated, Re and Cs are much depleted relative to their theoretical loadings based on the amounts removed during sludge synthesis. Se also falls under this heading but as none was detectable in the analyzed skydges a quantitative evaluation could not be entered in Table 6. At the other end of the spectrum are a number of values greater than one. If iron had been systematically leached from one mix then all the values down a column would be greater than 1, but this is not the case. Instead, each mix has a few values below 1 as well as a few greater than one. The most likely explanation is that the sludges were not homogeneous and that "nuggets" rich in particular elements cause these anomalous enrichments. Agglomerations of apatite crystals are one likely candidate. Support for this is found in the fact that the REDOX mix, which is devoid of Ca – and hence apatite, has only one value significantly in excess of 1 (Pb at 90° C, and a distinct Pb-containing phase was identified by TEM studies in this mix- Table II). Ba and Sr would also both fit into the apatite lattice. The fact that Ba but not Sr gives anomalous high values probably reflects the significantly greater removal of Sr from the Fe-Al oxide fraction of the sludge (Table IV). That is, even though a Sr-rich nugget might be included in a subsample enough Sr might be removed from the Fe and Al hydroxide gels so that the bulk analysis still gives an acceptably low ratio. There are also a variety of insoluble Nd phases (oxides, hydroxides, phosphates) that could form in these mixes and could account for account for the large number of "nuggets" associated with this element.

Retention of the remaining elements apparently is governed by sorption-desorption processes. Kinniburch, et al. (12) reviews the sorption of a variety of divalent cations onto freshly precipitated Fe and Al hydroxide gels (Table VII). These studies were carried out at room temperature and employed a 1m $NaNO_3$ 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 VII. 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 which are free of the apatite, and hence the nugget effects resulting in elevated Ba values. According to Table VII Ba is 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 VII - Relative releases of select divalent cations sorbed on freshly precipitated Fe^{+3} and Al^{+3} gels (from Kinniburch, et al., 12)

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

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 sites in unheated samples.

DISCUSSION

The essential issue is the degree to which these findings can be applied to the behavior of actual wastes. Though scant in comparison to the magnitude of the problem, the phase chemistry of actual tank sludges have been investigated to a limited degree (13). Principal Al-bearing phases likely to survive waste retrieval activities are tank are boehmite (typical of high temperatures) and gibbsite (lower temperatures). In Hanford tanks treated with diatomaceous earth or where other silica sources were provided (1) this material may be common. At Savannah River these same materials may also make up a significant amount of the heel in the tank bottoms (14) since zeolites used in Cs recovery were dumped in the tanks and subsequently altered to natrodavyne (a member of the cancrinite-family of zeolites). Iron occurs principally as amorphous iron hydroxide and as iron bismuth silicate hydroxide. Bi is also found as bismuth oxide and Cr is found associated with the both Al and Fe oxide – hydroxide components. Ca and P occur as hydroxyapatite.

Major phases identified in the artificial sludges (Table I) match this list quite closely. In general, the morphology of the synthetic iron oxides, hydroxyapatite, and zeolites are also quite similar to materials from the tanks (Fig. 1,2,3).

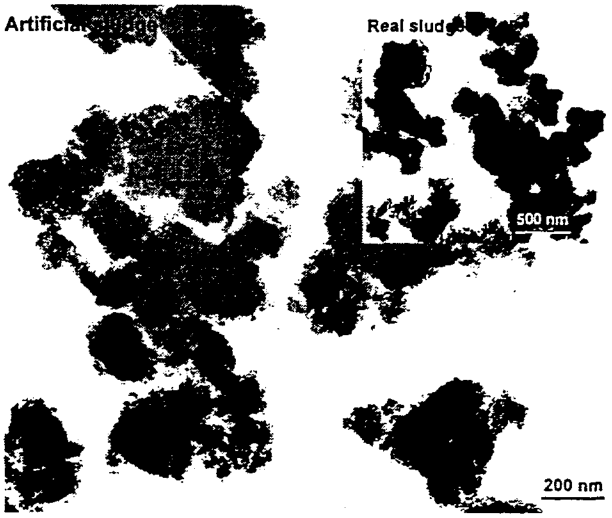
Artificial sludge containing dense agglomerates of Fe, Si, Bi has similar morphology to real tank waste (insert).

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Fig.1. Comparison of Fe >-Bi , Si oxides-hydroxide in synthetic and actual tank sludges (inset). Hydrous iron oxides without silica or bismuth have an identical appearance.

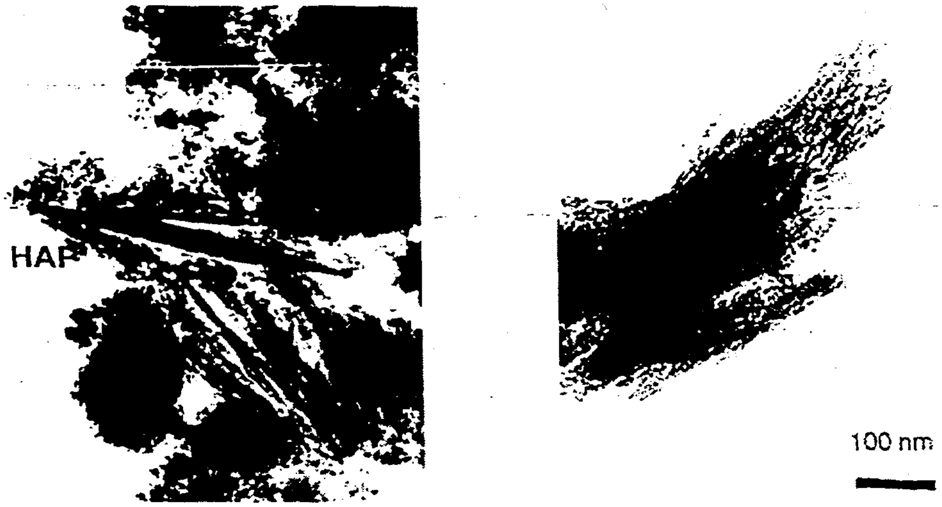

Fig. 2 Comparison of apatite from actual tank sludge (left) and artificial sludge (right).

Aluminosilicates in real tank waste and in artificial sludge have similar morphologies.

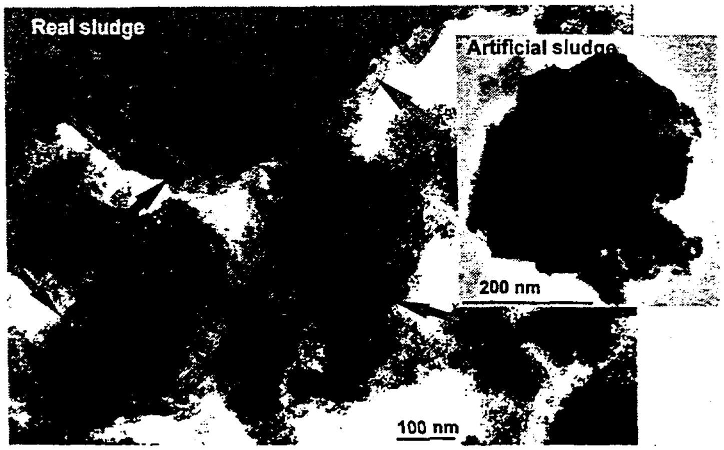

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Fig. 3 Comparison of zeolitic aluminosilicates in actual tank waste and synthetic sludge (inset)

For other phases there is not such a close match between artificial and actual materials. For example, although boehmite is the dominant Al-containing phase in both systems, the synthetic boehmite, is not nearly as well crystallized at material from the tanks (Fig. 4). Secondly, the synthetic iron bisumth oxides containing some silica appear identical to similar materials from the tanks (Fig. 1). But, we have failed to identify any iron bismuth silicate phase giving the poorly defined electron diffraction rings found in the actual Fe-Bi-Si rich tank sludges. Minor phases identified in real sludges, but not in the artificial mixes include Bi-chromate, Fe-Bi-phosphates, amorphous $Cr(OH)_3$, Fe-Mn oxides, La-phosphate, $(Fe,Mn)_2MnO_4$ and, of course, the occasional U or Pu containing oxide. However, given the complex chemistry of the Hanford tanks, it is evident that the artificial mixes have been remarkably successful at capturing the major phase chemistry of the sludges. By implication, it follows that the behavior of the radionuclide surrogates in these studies should provide at least a general picture of how a decommissioned tank will retain or release its radionuclides.

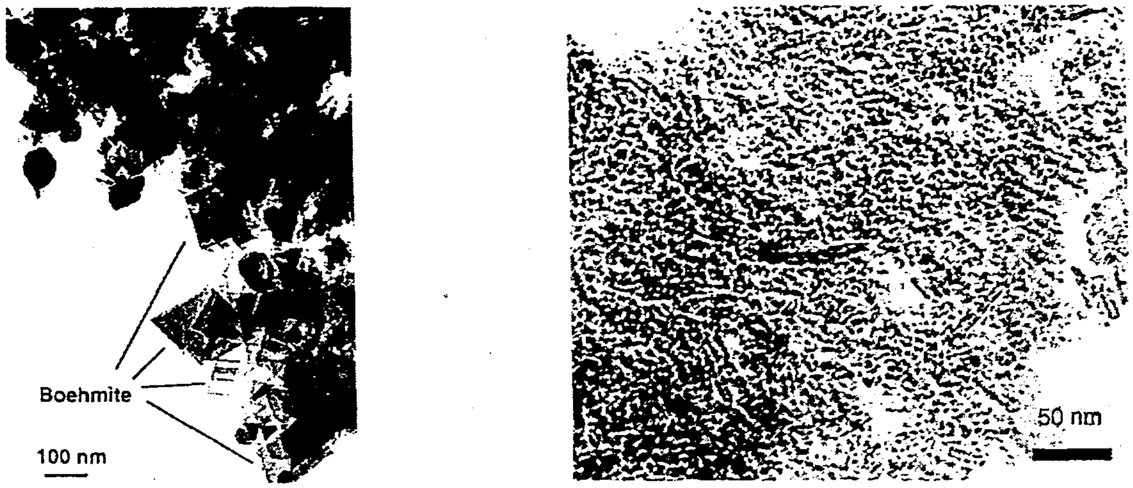

Fig. 4. Comparison of boehmite from actual tank wastes (left) and synthetic sludge (right)

The general behaviors governing the release or retention of surrogates are as follows:

1. Most of the chromate, Se, Tc and Cs inventory will probably leave with the first pulse of groundwater that permeates a mass of sludge. However, 10-20% of the inventory apparently will reside in the solid phases and be leached out more slowly.
2. In contrast, components like Am (e.g. Nd) and Pb should be essentially immobilized in the sludge unless the tank contents are exposed to groundwaters with pH values below neutrality.
3. Sr releases may be appreciable as the pH falls but Ba (e.g. Ra) will be retarded to a much greater degree.
4. Chromate will be highly mobile in sludges and the initial inventory of Cr^{+3} from stainless steel corrosion will oxidize to join chromate added as a process chemical.
5. Divalent metals such as Co and Cd will also be immobilized to a significant degree, but not quite as completely as Pb.

CONCLUSIONS

At this onset of this study it was unclear what, if anything, could be learned from the synthesis of artificial sludges. However, one accomplishment has been to demonstrate that the major phases likely to exist in tank sludges can, in fact, be produced artificially. Although the phase chemistry is generally correct the Al phases do not form the large boehmite crystals encountered in some tank sludges. Thus, chemical interdiction studies employing artificial sludges are likely to yield useful results employing these The use of artificial sludges to study the pumping properties of suspended tank sludges will, however, probably meet with less success. Finally, it has been established that prolonged aging of artificial samples is probably not necessary. A few weeks at near boiling generally seems to be sufficient to synthesize all the compounds likely to be found in actual sludges.

The ultimate goal of this study is being able to predict the release or retention of radionuclides by sludges. Significant progress has been made in working out the basic mechanisms governing these processes. Hydrous iron oxides evidently play a disproportionately role in this regard. This is not surprising and much of semiquantitative significance could be learned from the existing literature on the sorption/desorption properties of these materials as a function of solution chemistry. Hydrous aluminum oxides appear to play less of a role, but potentially could be important in explaining the retention of anions such as pertechnetate. In addition, solubility limits and dissolution rates for compounds like apatite and possibly rare earth phosphates may also provide important inputs to developing an overall radionuclide source term for use in performance assessments. Finally, even at this early stage into the investigation, it is apparent for certain radionuclides a large fraction of the inventory can safely be regarded as immobile under normal groundwater conditions.

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