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Lead Principal Investigator:

Dr. James L. Krumhansl
SMTS
Sandia National Laboratories - Albuquerque
MS-0750
P.O. Box 5800
Albuquerque, New Mexico 87185--0750
Telephone: 505-844-9093
e-mail: jlkrumh@sandia.gov

Co Principal Investigators:

Dr. Jun Liu
Pacific Northwest National Laboratory
Batelle Boulevard
P. O. Box 999
Richland Washington 99352
Telephone: 509-375-2616
e-mail: j_liu@ccmail.pnl.gov

Dr. Kathryn L. Nagy
Associate Professor
Department of Geological Sciences
University of Colorado
Campus Box 399
Boulder Colorado 80309 -0399
Telephone: 303-492-6962
e-mail: Kathryn.Nagy@Colorado.EDU

Patrick V. Brady
Sandia National Laboratories
Geochemistry Division, 6118
PO box 5800
Albuquerque New Mexico 87185 0750
U.S.A.
Telephone: (505) 844-7146
e-mail: PVBRADY@SANDIA.GOV

Aging Behavior of Simplified Hanford Waste Tank Sludges

Bradley Wakoff and Kathryn L. Nagy
University of Colorado
Department of Geological Sciences
Boulder, CO 80309-0399

Purpose

We are attempting to understand the solid phase chemistry of the high level nuclear waste (HLW) stored in tanks at Hanford. Because this waste is compositionally complex, our approach is to study experimentally the aging dynamics of simplified systems whose bulk chemistry approximates that of the tank sludges. After a basic understanding of these dynamics has been attained we plan to increase the compositional complexities one component at a time, in order to assess the influence of each component. Results will allow for reliable prediction of sludge phase chemistry over a range of sludge compositions.

Iron and aluminum comprise the bulk of most HLW sludges, so we chose to begin by studying the behavior of iron-aluminum systems. Fe/Al ratios were chosen to approximate those relevant to the solutions that produced the sludge. Aluminum and iron concentrations in the various process fluids are summarized and compared to our experimental starting solutions in [Table 1](#) (process solution data from Krumhansl, personal communication, 1998).

Our low aluminum experiments serve as direct analogues to both Bismuth Phosphate and low-Fe PUREX waste. Cornell and Giovanoli (1985) found that, in a pure iron system at 70°C, a 10-fold or even 50-fold increase in suspension concentration had only very slight effects on the final aged products. Since our experiments have similar Al/Fe ratios to some high Fe-PUREX process solutions our results are probably relevant to those wastes as well. However, our results may not apply to the high-Fe and high-Al PUREX wastes, as discussed below. The high Al experiments were designed specifically to simulate REDOX waste.

General Procedure

Experiments began with “neutralization” of iron (III)-aluminum nitrate solutions by addition of sodium hydroxide at room temperature. The final pH of most experiments was approximately 13.7. The samples were neutralized in PP or HDPE bottles that were then submerged in a water bath and aged at 90°C for up to 120 h. (In the low-Al systems, X-ray diffraction (XRD) results suggest that transformation of the initial amorphous precipitate to crystalline phases was complete after this time.) Experiments were run either as a single 250 mL sample (“single age experiments”) or as 2 L batches, from which 250 mL aliquots were drawn (“batch experiments”). Both solid phase chemistry and solution composition were monitored throughout the aging process. Samples were centrifuged and the experimental supernatant solutions were decanted and passed through a 0.4 μm syringe filter prior to analysis. Solids were dialyzed to removed excess salts. Aqueous Al and Fe were measured by the catechol violet (Dougan and Wilson, 1974) and Ferrozine (Dawson and Lyle, 1990) techniques, respectively. X-ray diffraction data were taken with a Scintag powder diffractometer scanning at 1° 2 Θ per minute using Cu K- α radiation and a graphite beam monochromator.

Results

The Low-Al System

The initial solid hydrolysis product formed in the low Al system is an amorphous iron phase, ferrihydrite. With time, this metastable phase transforms into the crystalline products hematite and goethite. The final proportions of hematite and goethite depend on the exact conditions under which the ferrihydrite is aged. In general, it has been found that high temperature favors hematite formation (Johnston and Lewis, 1983) while extreme pH (both high and low) favors goethite (Schwertmann and Murad, 1983). In the Hanford tanks (and in our experiments) these two effects compete with each other and both crystalline phases exist in the final products. Hematite appears to grow more quickly and becomes visible in the XRD data after 15 h, while goethite appears at 46 h (Fig. 1 and Table 2).

The solution composition data correlate well with the solid phase XRD data. Fe in solution was always below the analytical detection limit. In contrast, most Al in the system was in solution during the entire aging process (Fig. 2). The data show a distinct drop in aqueous Al at about 46 h of aging, coincident with the appearance of goethite. It has been shown that Al is more easily substituted into the goethite crystal structure (up to 33 mole percent; Schulze, 1984) than into the hematite structure (up to 16 mole percent; Schwertmann et al., 1979). The coincidence of the drop in aqueous Al with the appearance of goethite suggests that there is some uptake of aqueous Al by the nucleating goethite.

While the low-Al system behavior is generally consistent with trends found by other researchers, some work remains to be done. First, in an effort to further characterize the solids, quantitative XRD work could yield the final proportions of hematite and goethite as well as the distribution of Al in the solid phases. In addition, we plan to examine the partitioning behavior of rhenium (perrhenate, a surrogate for pertechnetate) with age among the aqueous, amorphous and crystalline phases in the system. However, it will be difficult, if not impossible, to distinguish between Re associated with the goethite and that associated with the hematite since it is very difficult to separate these two phases chemically or physically.

The High-Al System

Curiously, XRD analysis of the solid products of high Al systems revealed only ferrihydrite in the solid product (Fig. 3). With the exception of one experiment (to be discussed later), no solid Al-bearing phases were detected. Data based on Bayer Process solutions (Burkin, 1987) suggest that our experimental conditions (~ 4 M NaOH, 0.675 M Al) are well below Al(OH)₃ solubility at 90°C. It is possible that, even in the high Al REDOX waste, all the aluminum in the system is in solution. The only experiment in which a crystalline aluminous phase formed, experiment 135-3, had lower [OH] concentration and pH (13.1 vs. 13.7), suggesting that gibbsite solubility is a strong function of [OH] under these experimental conditions. If this is the case, we must re-examine how well our choice of solution compositions approximates the tank wastes.

Our experiments were run with total Al concentrations of 0.675 M. However, PUREX process solutions ranged from 0 to 1.32 M. These higher Al concentrations may supersaturate the waste solutions with respect to an aluminous phase. The presence of such a phase may have important effects on the solid-solution partitioning of the contaminants in the tanks and therefore requires further study.

Comparison of the high-Al experiment 135-4MB1' and the low-Al experiments 025B and 025B2 also reveals an important role of Al in the solid phase aging. These three experiments were all conducted in 4 M NaNO₃ and at pH ~ 13.7 (Table 2). In the low Al experiments, ferrihydrite transformation was detectable after 15 h and appears to be complete by 96 h. However, there is no detectable crystalline iron phase present in batch 135-4MB1' even after 95 hours of aging. This trend is also observed in experiment 8-1, conducted at a slightly lower Al/Fe value. Aluminum impedes the transformation of the amorphous iron precipitate. Ferrihydrite is known to be an effective metal sorbent; therefore, its presence in the

Hanford waste tanks may substantially affect the solid-solution distribution of radionuclides and other metal contaminants. Chemical and AFM analysis of these ferrihydrite particles should yield information about the mechanism by which this transformation proceeds. Knowledge of the transformation mechanism is needed for predicting the potential for further transformation and the subsequent release of sorbed or occluded metals.

Future Work

Further analytical work remains to be carried out on the experiments we have already conducted, as described above. In addition, we plan to develop a more robust understanding of the sludge phase chemistry by conducting additional sets of experiments. As previously alluded to, we plan to examine the partitioning behavior of Re as a surrogate for Tc. In addition, there is reason to suspect that additional chemical components may substantially influence the phase chemistry of the crystalline solids. Co-workers at Sandia National Laboratories have found a layered-double-hydroxide reevesite-like phase in more complex synthetic sludges (Krumhansl, personal communication, 1998). For this reason, we plan to examine the influence of divalent cations (Mn and Ni) on the phase chemistry of the sludges.

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Table 1. Comparison of solutions used in reprocessing with experimental conditions

	[Fe] (mol/L)	[Al] (mol/L)	[Al]/[Fe] (mol/mol)
<u>Reprocessing Technology:</u>			
TBP U-Recovery	1.6×10^{-2}	0	0
Bismuth Phosphate	3.15×10^{-2}	0 to 8.25×10^{-2}	0 to 2.62
REDOX	4.8×10^{-2}	0.648	13.5
PUREX (Kupfer et al., 1997)	0.4	0 to 1.32	0 to 3.3
PUREX (from Cleveland, 1967)	0.04 to 0.06	0	0
<u>Experimental Compositions:</u>			
low Al composition	0.05	0.0125	0.25
high Al composition	0.05	0.675	13.5

Table 2. Experimental Results*

Sample ID	Al/Fe (mol/mol)	mol percent	[NaNO ₃] (M)	Final pH	aging time (hrs)	solid phases
025-0	0.25	20% Al	4	13.49	0	fh
025B-8	0.25	20% Al	4	not measured	8.43	fh
025B2-15	0.25	20% Al	4	not measured	15.18	fh, hem
025B2-23	0.25	20% Al	4	13.79	23.13	fh, hem
025B2-33	0.25	20% Al	4	13.71	32.83	hem, fh
025B-46	0.25	20% Al	4	13.77	46.38	hem, gt, fh
025B2-60	0.25	20% Al	4	13.65	60.37	hem, gt (fh?)
025B-120	0.25	20% Al	4	13.69	120.4	hem, gt
8-1	8.0	11.1% Fe	4	not measured	21.9	amrph, fh, peak at 29.2° 2θ
13.5-1	13.5	6.9% Fe	0	13.35	24.58	amrph, fh
13.5-2	13.5	6.9% Fe	0	13.35	47.48	amrph, fh, (hem), peak at 29.2° 2θ
13.5-3	13.5	6.9% Fe	4	13.16	27.53	gb, (hem), peak at 29.2° 2θ
135-4MB1-4	13.5	6.9% Fe	4	13.63	4.05	amrph, (fh?)
135-4MB1-23	13.5	6.9% Fe	4	13.59	23.05	amrph, (fh?)
135-4MB1-95	13.5	6.9% Fe	4	13.52	95.03	amrph, (fh?)
135-2MB1-4	13.5	6.9% Fe	2	13.77	4.06	amrph, (fh?)
135-2MB1-23	13.5	6.9% Fe	2	13.72	23.0	amrph, (fh?)
135-2MB1-95	13.5	6.9% Fe	2	13.68	95.28	amrph, (fh?)

fh = ferrihydrite; gt = goethite; hem = hematite; gb = gibbsite; amrph = amorphous solids

Samples with a "B" in the Sample ID are batch experiments, all others are 250 ml single-age experiments.

*Analyses from intermediate times in experiments 025B and 025B2 omitted for brevity.

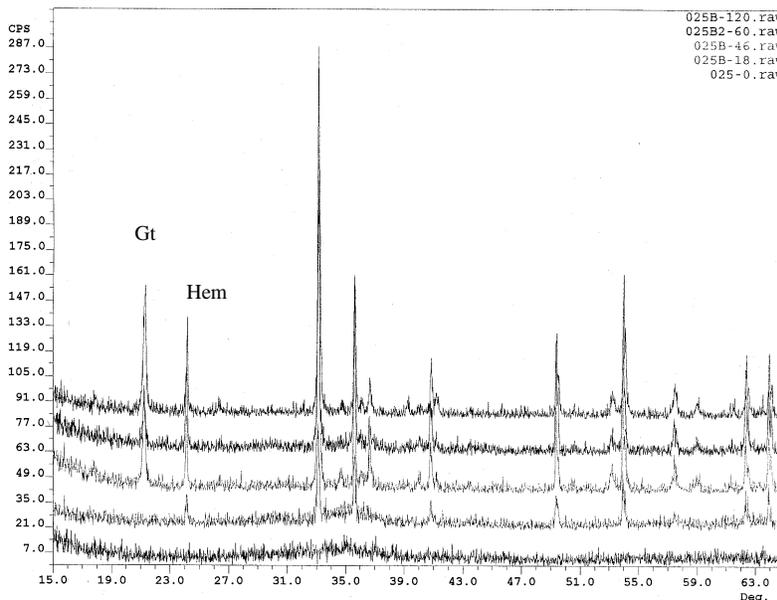


Figure 1. Selected XRD data from experiments 025B and 025B2. The labeled hematite and goethite peaks are the largest peaks for each phase that do not overlap. Goethite appears at 46 h aging but hematite appears much earlier at 15 h. The ages of the patterns (from top to bottom) are 0 h (no aging), 18 h, 46 h, 60 h and 120 h.

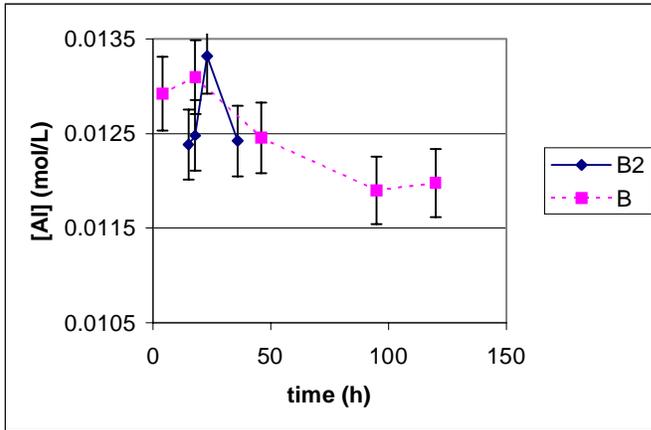


Figure 2. Aqueous aluminum concentration vs. aging time from experiments 025B and 025B2. Al concentrations peak after 23 h, then drop. The timing of this drop corresponds with the appearance of goethite. The initial increase is likely due to dissolution or leaching of solid-phase aluminum precipitated during “neutralization” of the sample. Error bars show +/- 3%.

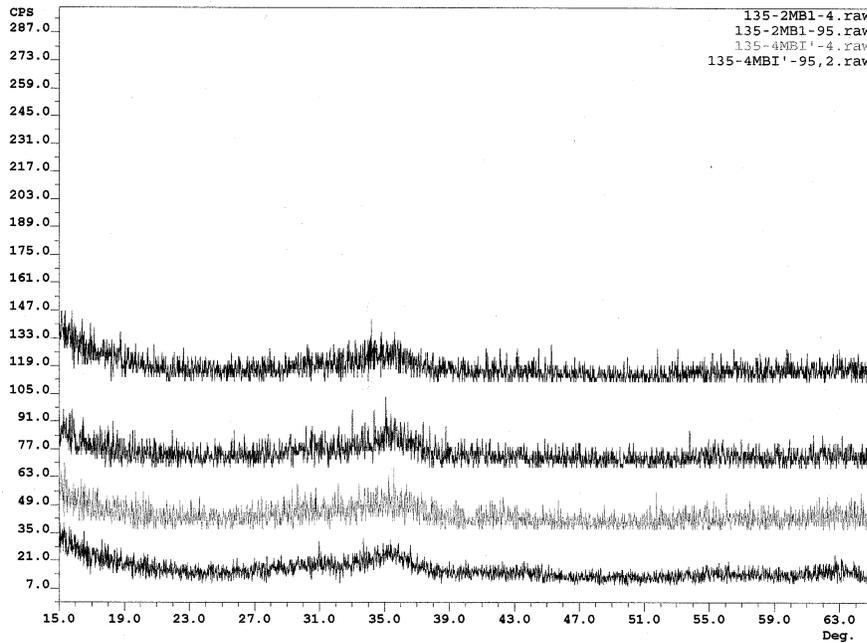


Figure 3. Selected XRD data from the high-Al experiments 135-2MB1 and 135-4MB1'. In both experiments, the amorphous iron oxyhydroxide ferrihydrite (large broad peak centered at $\sim 35^\circ 2\theta$) was the only phase detectable. The ages of the patterns are (from bottom to top): 95 h in 4 M NaNO_3 , 4 h in 4 M NaNO_3 , 95 h in 2 M NaNO_3 , and 4 h in 2 M NaNO_3 .