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Boehmite Actual Waste Dissolution Studies

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Abstract: The U.S. Department of Energy plans to vitrify approximately 60,000 metric tons of high-level waste (HLW) sludge from underground storage tanks at the Hanford Nuclear Reservation. To reduce the volume of HLW requiring treatment, a goal has been set to remove a significant quantity of the aluminum, which comprises nearly 70 percent of the sludge. Aluminum is found in the form of gibbsite, sodium aluminate and boehmite. Gibbsite and sodium aluminate can be easily dissolved by washing the waste stream with caustic. Boehmite, which comprises nearly half of the total aluminum, is more resistant to caustic dissolution and requires higher treatment temperatures and hydroxide concentrations.

Samples were taken from four Hanford tanks and homogenized in order to give a sample that is representative of REDOX (Reduction Oxidation process for Pu recovery) sludge solids. Bench scale testing was performed on the homogenized waste to study the dissolution of boehmite. Dissolution was studied at three different hydroxide concentrations, with each concentration being run at three different temperatures. Samples were taken periodically over the 170 hour runs in order to determine leaching kinetics. Results of the dissolution studies and implications for the proposed processing of these wastes will be discussed.

Keywords: Boehmite; Hanford; HLW; Plant; Tank waste; Waste treatment

INTRODUCTION

Approximately 60,000 metric tons of high level waste (HLW) sludge is currently contained in 177 underground storage tanks at the Hanford Nuclear Reservation in Richland, Washington. The U.S. Department of Energy plans to vitrify the sludge, which is composed of solids in

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the waste that have settled to the bottom, into a glass waste form for disposal in a geologic repository. As much as 70% of the sludge is composed of aluminum. Chromium is a minor component (~3%) of the sludge. The Hanford Waste Treatment Plant (WTP) has a processing target to remove significant aluminum such that it is no longer the waste-limiting component in the final HLW glass waste form. The chromium must also be removed before producing the glass waste forms because there is a low tolerance for chromium in the HLW immobilization process. The undesirable HLW sludge components such as aluminum and chromium will be removed by leaching with NaOH before glass formation. Successfully completing these objectives will allow a factor of nearly two reduction in the quantity of HLW glass that will be produced in the WTP.

All of the solids remaining after leaching will be processed as HLW, consequently identifying the effect of process variables such as temperature and hydroxide concentration will allow better understanding of and control over the volume of solids requiring vitrification as well as the quantity of HLW glass formed. Nearly half of the aluminum in the tanks is found as boehmite (AlOOH), with the remainder being gibbsite ($Al(OH)_3$), sodium aluminate ($NaAlO_2$), and a small amount of alumino-silicate materials

Gibbsite and sodium aluminate are easily dissolved by heating under caustic conditions (e.g., 8 hours at 50°C with 3 M NaOH). Boehmite requires more aggressive conditions of higher temperatures and longer times to dissolve (1). Boehmite dissolves according to Equation 1 (2).

$$AlOOH + OH^- + H_2O \leftrightarrow Al(OH)_4^- \tag{1}$$

In order to study the dissolution of boehmite in a variety of Hanford tanks, several tanks with a predominant boehmite component were targeted for testing. To this end, REDOX waste, high in aluminum and subjected to high temperature as a result of the storage condition was identified as most likely to contain boehmite. Samples from four tanks were chosen.

EXPERIMENTAL

Analytical Methods

Metals Analysis

Metals were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES).

Anions

Anions were determined by ion chromatography using a Dionex ICS-2500 IC system equipped with a conductivity detector.

Free Hydroxide

The free hydroxide was determined using potentiometric titration with standardized HCl on a Brinkman 636 Auto-Titrator.

KOH Fusions

The KOH fusion was conducted in the shielded analytical facility (hot cells). A nominal sample size of 0.1 to 0.2 g dry solids was combined with a KOH/KNO_3 flux mixture and fused at 550°C for one hour in a nickel crucible. The fused material was acidified with HNO_3, taken to a 100-mL volume with DI water, and then split for metals and radionuclide analysis.

Uranium

Total uranium was determined directly, from samples prepared by KOH fusion, using a Chem Chek Instruments Kinetic Phosphorescence Analyzer (KPA).

Gamma Energy Detection

Sample counting was conducted with Gamma Energy Analysis (GEA) using high purity germanium detectors. Extended count times (up to 20 h) were employed as needed to achieve low detection limits.

Particle Size Distribution

Particle Size Distribution (PSD) characterization used a Mastersizer 2000 (Malvern Instruments, Inc., Southborough, MA 01772 USA) with a Hydro µP wet dispersion accessory. The PSD measurements were conducted on the washed solids in a 0.01 M NaOH dispersion solution matrix. The sample dispersion was added drop-wise to the instrument (while the pump was active) until a ~10% obscuration was reached.

X-Ray Diffraction (XRD)

The sample mounts for XRD determination were prepared from the dried solids. Specimens were ground to small mesh size, mixed with internal standard (rutile (TiO_2), or alumina (Al_2O_3)), and mounted on a glass slide. The X-ray powder pattern of the washed tank solids were obtained on a (Sintag Pad V, $\theta/2\theta$ configuration) from 5 to 65 degrees 2θ, with a step size of 0.02 degrees and a dwell time of 20 seconds. Phase identification was processed with JADE, Version 8.0 (Materials Data Inc., Livermore, CA) software search and peak match routines with comparison to the ICDD (International Centre for Diffraction Data) database PDF-2, Version 2.0602 (2006). The ICDD database included the ICSD (Inorganic Crystal Structure Database) maintained by Fachinformationszentrum, Karlsuhe, Germany. Phase identification incorporated chemistry restrictions based on the elements determined from chemical analysis.

SEM

A small sample was transferred with a wooden Q-tip stem onto carbon tape supported by an aluminum pedestal mount. The sample was analyzed using the radiation-shielded Amray Model 1610T SEM. In selected cases, the mount was carbon-coated. Selected sample areas were evaluated by Energy Dispersive Spectroscopy (EDS) for qualitative elemental composition.

Preparation of REDOX Sludge Solids

A composite sample was generated from multiple smaller samples. The relative ratio of tanks (on a mass basis) is represented in Fig. 1. The dried samples were scraped out into a stainless steel pan and crushed. All materials were then passed through a 1/8″ pore size stainless steel mesh screen fitted to the top of the compositing vessel to capture large materials (e.g., rocks). All tank waste materials successfully passed through the screen. Deionized water was used to aid the transfer and hydrate the solids.

The wetted solids were mixed for 1 h in a 5-L stainless steel baffled vessel equipped with an overhead double-bladed impeller. The solids were then covered and allowed to hydrate overnight. The hydrated solids were stirred for ~10 min and then subdivided into sample jars. The sludge composite was a thick, gray slurry with a minimal separable aqueous layer.

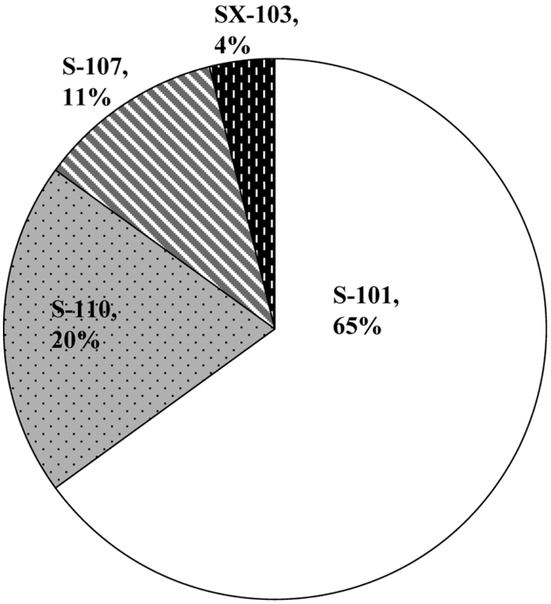


Figure 1. Relative ratio of components in blended composite.

Washing of Sludge Solids

A 100-g slurry of the homogenized composite sample was centrifuged (at ~960 G) for 20 minutes, and the supernatant was removed. The solids volume was estimated to be 37 mL. Approximately 110 mL (3 × the centrifuged solids volume) of 0.01 M NaOH was added and the slurry was mixed for 15 minutes using an overhead mixer. The slurry was centrifuged (at ~960 G), and the supernatant removed. The wash steps were repeated twice for a total of three washes.

The solids were thinned in deionized water and the slurry was subdivided into one 60-mL HDPE bottle and thirteen 125-mL HDPE bottles, each containing 1.25 grams of water insoluble solids. A slurry sample containing 0.4 g of solids was submitted for analysis by ICP-OES, XRD, and SEM. A solution of 10 M NaOH was added to each of the thirteen samples, then diluted to 100 mL with deionized water to adjust the NaOH concentration in each of the samples to support the test matrix shown in Table 1. The test matrix evaluated the effects of free hydroxide concentration (1 to 5 M NaOH), temperature (80 to 100°C), and sodium nitrate concentration (1 to 5 M $NaNO_3$) on boehmite leaching kinetics. Limited sample was available for testing, so it was decided

Table 1. Caustic leaching conditions

Free [OH^-], M		[NO_3^-], M		Temperature, °C
Target	Measured	Target	Measured	
1	0.97	NA	NA	80
3	3.30	NA	NA	80
5	5.06	NA	NA	80
1	0.91	NA	NA	90
3	2.94	NA	NA	90
3	2.90	NA	NA	90
3	3.02	NA	NA	90
3	3.13	1	1.11	90
3	3.06	5	5.13	90
5	5.01	NA	NA	90
1	0.86	NA	NA	100
3	2.81	NA	NA	100
5	5.11	NA	NA	100

that triplicate samples for only 1 condition would be run to determine the accuracy of the experiment. This was done at the median temperature and hydroxide conditions (90°C and 3 M NaOH).

Batch Contacts

Temperature was controlled by an aluminum heating block (J-KEM Scientific, Inc.) equipped with a Type T thermocouple. The heating block was supported on a J-KEM BTS-3500 digital bench top shaker. The samples were grouped according to the leach temperature. Before the leach testing of each group was conducted, the heating block was pre-heated to the appropriate temperature.

The leaching mixtures were shaken for 170 hours at 200 rpm. Visual inspection indicated this mixing speed effectively suspended the particles uniformly in solution. Solution samples were withdrawn at 1, 4, 8, 24, 72, and 170 hours. At each sampling time, the shaker was stopped, and the solids were allowed to settle. Approximately 2-mL of the clarified leachate was withdrawn with a 5-mL syringe, and filtered through a 0.45 μm nylon syringe filter; both the syringe filter and the syringe were pre-heated in an oven to 100°C prior to filtering. One 0.5-mL sample of filtered leachate was acidified with 15 mL of 0.3 M HNO_3 for analysis by ICP-OES, and another 0.5-mL sample of filtered leachate was added to 15 mL of 1E-04 M NaOH for analysis by ion chromatography. The remaining filtered solution was returned to the leaching vessel, and leaching was continued. The new liquid level was marked after each sample was taken. Evaporation was minimal during the course of the experiment. If evaporation occurred between sampling times, the sample volume was returned to the previous sample level by addition of deionized water. After 170 hours, the slurries were removed from the mixing/heating block and cooled to ambient (~22°C) temperature. Samples were taken for analysis of free hydroxide and for GEA. One sample was also taken for analysis of Cr(VI) by visible spectrophotometry (diluted into 0.1 M NaOH). The values for free hydroxide and nitrate shown in Table 1 are results from the samples taken at 170 hours. The slurries were centrifuged, and the solids were completely transferred to tared 15-mL centrifuge tubes. The samples were then centrifuged, the leachate removed, and the centrifuged solids volume and wet mass determined for each sample.

The solids from the triplicate samples leached at 90°C in 3 M NaOH were prepared for analysis of the solids. One of the solid samples was slurried in 0.01 M NaOH and divided between the remaining two solid samples. These two solid samples were then washed three times in 0.01 M NaOH. Approximately 5 mL of 0.01 M NaOH was added to each centrifuge tube and mixed on a vortex mixer for 5 minutes. The slurries were centrifuged for 5 minutes and the supernatant removed. The wash steps were completed twice for a total of three washes. After the final wash, the two samples were combined into one centrifuge tube by slurrying in additional 0.01 M NaOH. The sample was centrifuged and the supernatant removed.

RESULTS AND DISCUSSION

Analysis of Initial Washed Sludge Solids

The washed REDOX solids chemical composition was determined by ICP-OES and is provided in Table 2. As expected, the sludge consisted primarily of aluminum with significant sodium and uranium components. The supernatant was primarily sodium nitrate and sodium nitrite. A mass/charge balance was evaluated for the Al^{3+}, Na^{+}, OH^{-}, NO_3^{-}, NO_2^{-}, and CO_3^{2-} in the supernatant and resulted in good agreement (2.4%).

The XRD pattern of the initial washed REDOX solids is shown in Fig. 2. The XRD pattern was dominated by boehmite with minor contributions from gibbsite, iron oxide, sodium nitrate, and sodium uranium oxide. A small amount of talc was found in the sample and was traced

Table 2. Chemical characterization of the initial REDOX sludge

Analyte	μg/g
Al	388,250
Cr	1,733
Fe	8,463
Mn	5,375
Na	55,200
Ni	308
Si	15,250
Sr	1,243
U	21,750

to contamination from the powdered gloves used in the sample preparation. Boehmite is known to dissolve much more slowly than gibbsite (1). The XRD of the initial washed solids shows the sample to be 75.5% boehmite with only 5.8% gibbsite remaining after the wash procedure, as determined by the software. The values are derived from peak area and RIR (Relative Intensity Ratio) data.

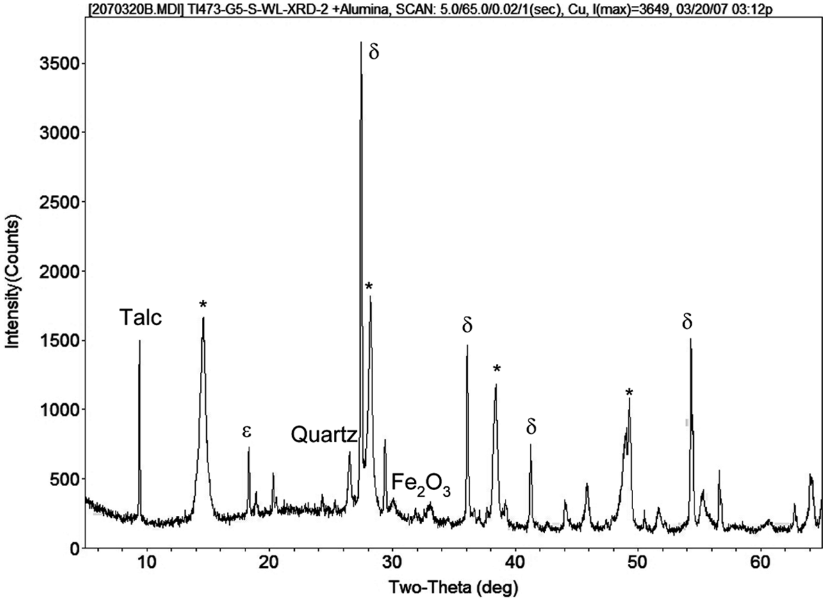


Figure 2. XRD pattern of washed REDOX sludge, background-subtracted *Boehmite, δ TiO_2, ε Gibbsite.

Table 3. Washed REDOX sludge phase composition (entrained supernatant removed)

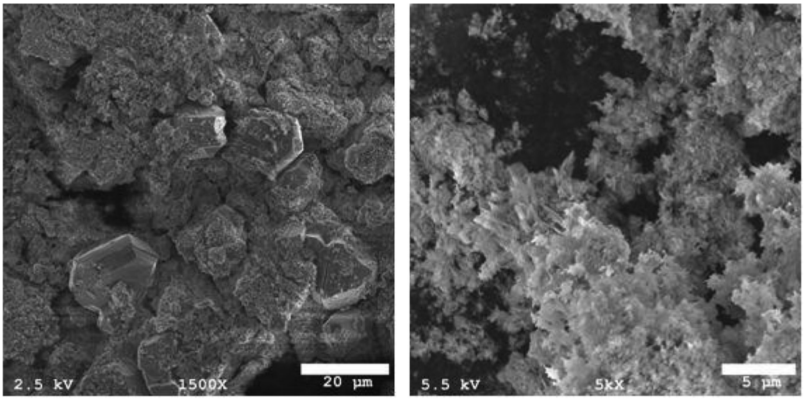
Crystalline phase	Chemical structure	Weight %	Basis
Boehmite	$AlOOH$	77.5	Observed
Gibbsite	$Al(OH)_3$	5.8	Observed
Sodium uranium oxide	$Na_2U_2O_7$	2.6	Observed
Iron oxide	Fe_2O_3	1.0	Observed
Manganese dioxide	MnO_2	0.71	Assigned
Unaccounted sodium	Na (in Al matrix)	4.7	Assigned
Chromium hydroxide	$Cr(OH)_3$	0.42	Assigned
Nickel hydrogen phosphate hydrate	$Ni(H_2PO_2)_2(H_2O)_6$	0.16	Observed
Strontium oxide	SrO	0.14	Assigned
Entrained Na salts from supernatant	various	5.0	Observed
Sum		98.0	

The XRD pattern was consistent with the chemical analysis. The approximate mass percent of the chemical phases was estimated by evaluating the crystalline species in conjunction with the elemental concentrations. Nominally 90 wt % of the solids was identified; ~7% of the sodium content could not be tied to a specific phase. Trivalent chromium and iron, tetravalent manganese and silica are insoluble under the basic conditions of the wash. The nickel and uranium phases as identified by XRD are likewise fairly insoluble. The high sodium content may have been present possibly from incomplete removal of hydroxide and nitrate during the wash cycles, as suggested by the presence of sodium nitrate in the XRD powder pattern (Fig. 2). In order to include the strontium and manganese identified by ICP, $SrCO_3$ and manganese dioxide are included in the speciation map, shown in Table 3, as possible insoluble candidates.

SEM images of the washed solids are shown in Fig. 3, showing agglomerates of small particle-sized materials, suggestive of a high surface area sample. These images support the PSD analysis that indicated particle diameters were largely on the order of 10 μm with a range of 0.2 to 40 μm. However, the primary boehmite crystals appear to be much smaller and overall the particles appear to be made up of aggregates of boehmite crystals and other amorphous constituents.

Leaching Performance

Plots of the Al dissolution behavior at 80, 90, and 100°C are shown in Figs. 4, 5, and 6, respectively. At 80°C, the dissolution of Al was similar



(a) (b)

Figure 3. SEM images of the initial washed REDOX sludge.

in the 3 and 5 M NaOH, but less dissolution was seen in 1 M NaOH. Within the first 8 hours of the test, there was a fairly quick rise in Al concentration, up to about 1,500 μg/g in 3 and 5 M NaOH, there was also a fast rise in 1 M NaOH, but only up to about 1,200 μg/g. After 8 hours, the rise in concentration slowed under all three conditions. Concentration

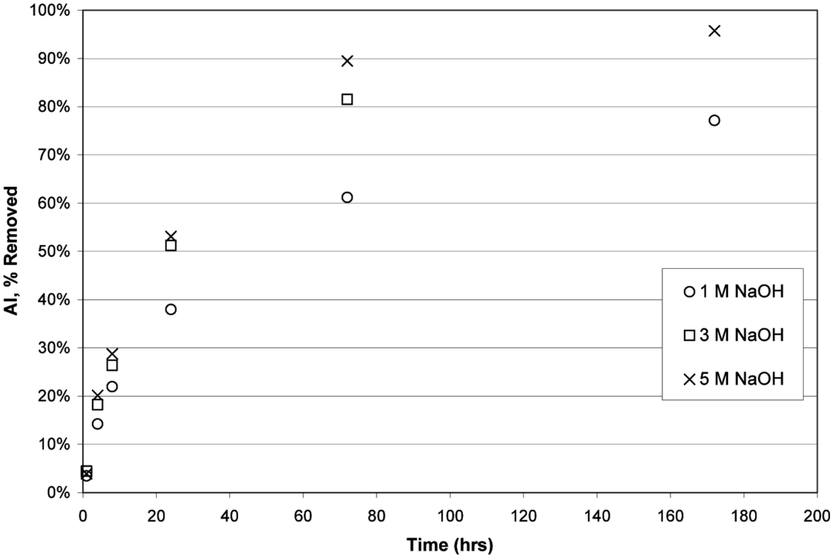


Figure 4. Aluminum concentration in the leachate as a function of time at 80°C.

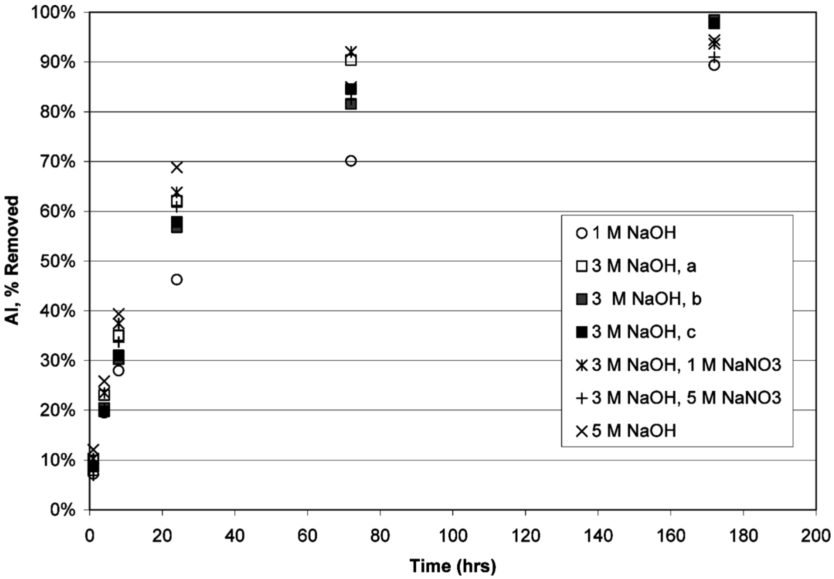


Figure 5. Aluminum concentration in the leachate as a function of time at 90°C.

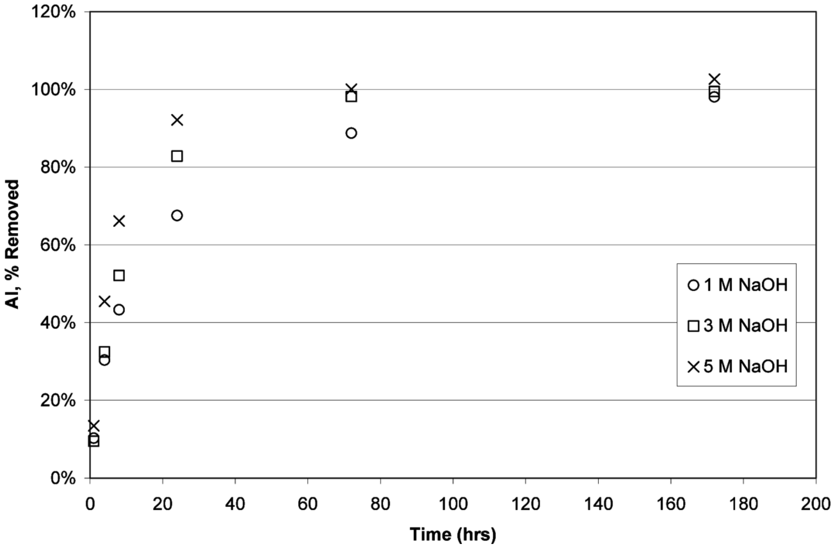


Figure 6. Aluminum concentration in the leachate as a function of time at 100°C.

in the 3 M NaOH sample lagged just a bit behind the 5 M sample, and the rise in the 1 M sample was the slowest, even after 170 hours it remained about 1,000 μg/g below the concentration found in the 3 M NaOH sample. The dissolution of Al appears to be complete at 170 hours in 3 and 5 M NaOH, reaching 101 and 96% dissolution, respectively. Complete dissolution was not obtained in the 1 M NaOH sample, reaching only 77% of completion. The rapid rise in Al concentration at early times is probably due to the fact that gibbsite was dissolving, and later times saw the commencement of the boehmite dissolution.

Under the seven conditions at 90°C shown in Table 2, there was a rapid rise in Al concentration during the first 8 hours of the test, up to 1,500–2,000 μg/g. After eight hours, the concentration continued to rise under all test conditions, but at a slower rate. The dissolution in 1 M NaOH lagged behind that of the samples in 3 and 5 M NaOH at 24 and 72 hours, but reached nearly the same level of dissolution after 170 hours. At 170 hours, the triplicate samples agreed very well with one another, with an average of 5,346 ± 19 μg/g Al in solution. The dissolution was nearly complete in the triplicate samples run in 3 M NaOH, each reaching 98% completion. The sample run in 1 M NaOH only reached 89% completion. The addition of excess sodium did not result in increased dissolution of aluminum.

Both the sample in 5 M NaOH and the sample in 3 M NaOH with additional 1 M $NaNO_3$ reached 94% completion, whereas the addition of 5 M $NaNO_3$ to the sample in 3 M NaOH only reached 91% completion after 170 hours.

At 100°C, the dissolution was much faster in the first 8 hours than seen at lower temperatures. Initially, a greater variance in the amount of Al dissolved was observed at 1, 3, and 5 M NaOH in the first 24 hours of testing than was seen at 80 and 90°C. However, at 72 hours, the 3 and 5 M NaOH samples showed nearly the same amount of Al dissolved, and at 170 hours, all three conditions showed about the same amount of dissolution. The 1 M sample reached 98% completion, and the 3 and 5 M samples reached 100% completion after 170 hours.

Leached Solids Characterization

Table 4 shows the percentage of aluminum that was removed at each leaching condition after leaching for one week. The removal of aluminum increased with either increased temperature or hydroxide concentration.

Solids that had been caustic leached at 90°C in 3 M NaOH were slurried in deionized water and sub-divided for analysis by PSD, XRD, SEM, and ICP. The ICP results for the initial untreated solids and the solids

Table 4. Percent of Al removed after 1 week of leaching

Temp, °C	[NaOH], M	[NaNO$_3$], M	% Al Removed
80	0.97	NA	77
80	3.30	NA	101
80	5.06	NA	96
90	0.91	NA	89
90	2.94	NA	98
90	2.90	NA	98
90	3.02	NA	98
90	3.13	1.11	94
90	3.06	5.30	91
90	5.01	NA	94
100	0.86	NA	98
100	2.81	NA	100
100	5.11	NA	103

that were leached for 170 hours can be seen in Table 5 along with the leach factors (Wt %) of the main constituents.

The ICP analysis of the leachate solutions showed that Mn, Sr, and U had not dissolved during leaching. The relative concentration factor (CF) of these analytes averaged 12 in the final leached and washed solids, based on the concentration ratio after leaching to before leaching. This term was used to determine the specific analyte leach factors according to Equation 2

$$LF = \left(\frac{C_F}{C_1 \times 12}\right) \tag{2}$$

Table 5. Solids inventory and percent leached

Analyte	Initial solids inventory, µg/g	Inventory after leaching, µg/g	Percent leached
Al	388,250	83,675	98.3
Cr	1,733	9,770	54.3
Fe	8,463	73,825	29.2
Mn	5,375	62,650	0
S	3,611	4,100	90.8
Si	15,250	17,875	90.5
Sr	1,243	15,125	0
U	21,750	286,750	0
Ca	9,100	22,975	79.5

where LF = leach factor
C_F = final analyte concentration
C_I = initial analyte concentration.

As shown in Fig. 7, approximately 90% of the mass dissolved with a 170-hr leach time. Uranium would become the limiting component of the glass loading.

The background-subtracted XRD pattern with stick-figure phase identification is shown in Fig. 8. The major crystalline phase identified in this sample was clarkeite, $Na[(UO_2)O(OH)]$. The clarkeite XRD pattern is very similar to that of sodium uranium oxide [$Na_2U_2O_7$], but the clarkeite pattern resulted in a slightly better fit to the data. The presence of boehmite was strongly suspected but could not be confirmed. The boehmite major peak was indicated in the 15-degree peak by the non-symmetrical low-angle side of the peak. Most of the remaining boehmite peaks were either masked by other phases or at such low intensity that they could not be identified. The clarkeite phase has a much higher RIR (Relative Intensity Ratio) than boehmite, so the boehmite contribution was not readily apparent. A very low intensity signal (only 2 lines observable) could be strontium manganese oxide hydrate, $Sr_2Mn_{14}O_{27}·xH_2O$. Due to the very low peak intensity and the lack of sufficient confirming lines, the identification of this phase must be regarded as tentative. The pattern for this sample indicated that the

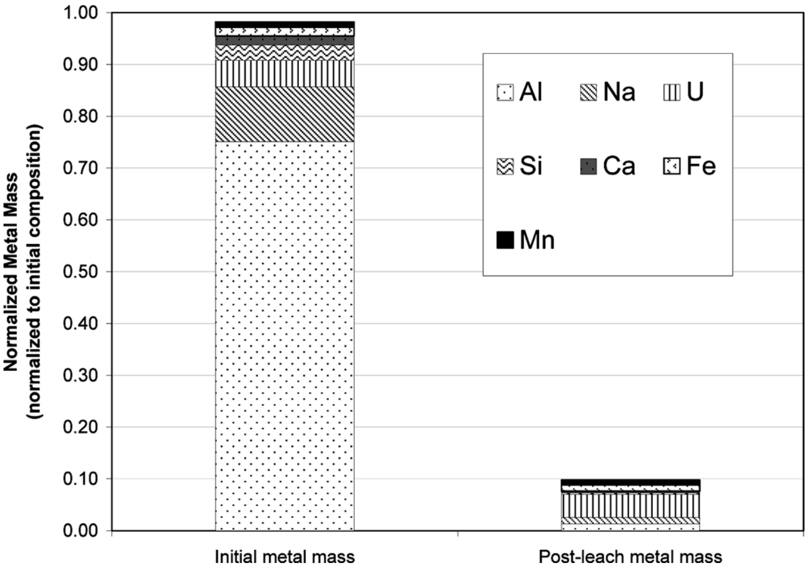


Figure 7. Reduction in solid mass with caustic leaching.

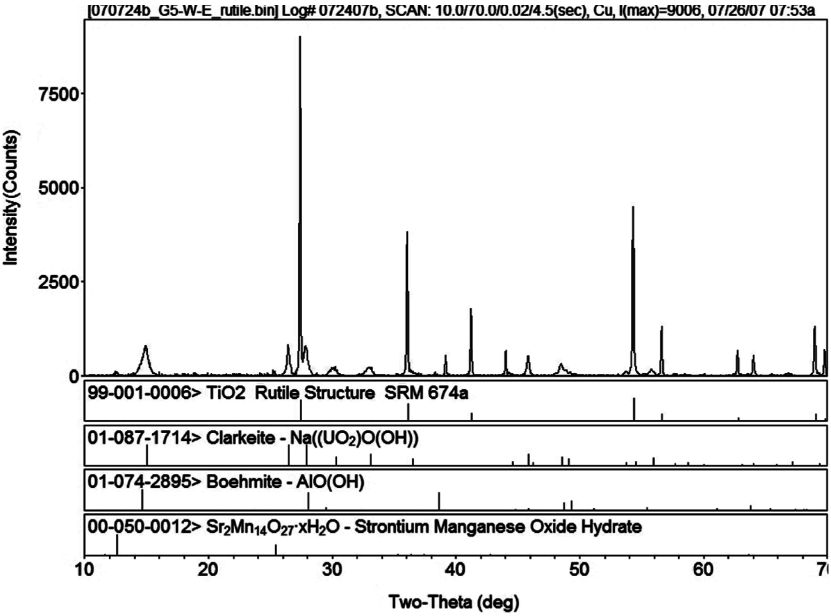


Figure 8. XRD pattern of caustic leached REDOX sludge, background-subtracted with stick-figure peak identification.

material was mostly amorphous. The result confirms the amorphous and insoluble nature of the initial washed solids.

Relevance to Glass Loading

Aluminum is the limiting component for Group 5 waste loading in glass. After 95 wt% of the Al is removed U becomes the limiting component for waste loading. Therefore, as Al is leached from the Group 5 waste, the product HLW glass mass will decrease. The mass of HLW glass produced relative to the starting Group 5 waste composition *and* as a function of waste mass can be estimated from the fraction of Al removed from the solids phase as shown in Equation 3.

$$\frac{\text{g glass}}{\text{g solids}} = \frac{(1 - \mathrm{F_{Al}}) * \frac{\mu\text{g Al}}{\text{g solids}} * \frac{\text{g}}{\text{1E6}\mu\text{g}} * \frac{1.89\ \text{g Al}_2\text{O}_3}{\text{g Al}}}{\frac{0.11\text{g Al}_2\text{O}_3}{\text{g glass}}} \tag{3}$$

where $\mathrm{F_{Al}}$ = fraction of dissolved Al (varies as a function of leach time)
μg Al/g solids = Al concentration in starting solids fraction (388,000 μg/g)
0.11 g Al_2O_3 = contract limit for Al_2O_3 loading into waste glass

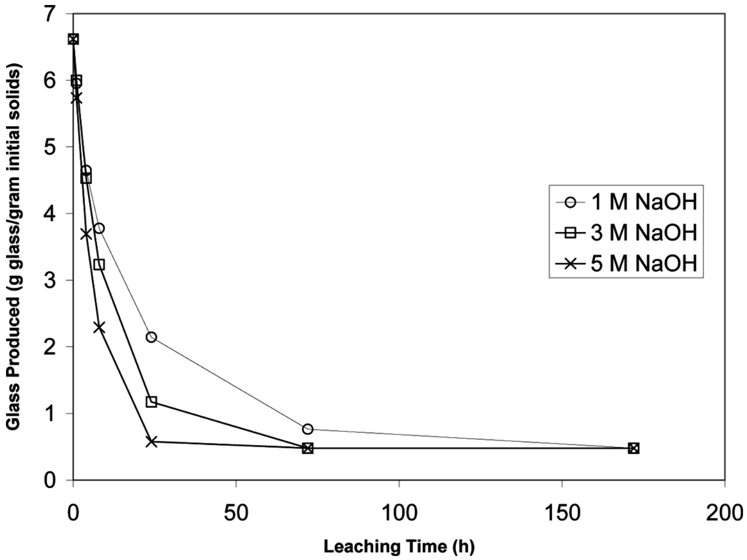


Figure 9. Reduction in glass produced as a function of leach conditions and time.

This equation was used to calculate the grams of glass produced per gram of initial solids as a function of leaching time at 100°C and at 1, 3, and 5 M NaOH concentrations. As shown in Fig. 9, the majority of the reduction in glass production can be achieved with a 24-hr leach time, with nearly a ten-fold reduction in glass volume produced.

CONCLUSIONS

Based on the results of these tests, the adequate dissolution of boehmite from waste from the Hanford tank farms can be achieved in approximately 24 hours using a 3–5 M NaOH solution at 100°C. Further, these test results indicate limited likelihood that other anions such as nitrate will significantly affect the dissolution rate for these wastes. These results also suggest that the reaction rate is relatively insensitive to the hydroxide ion concentration in the starting slurry. The results also suggest that temperature will affect the reaction rate. The dissolution rate appears to approximately double every 20 degrees of temperature increase. The residual solids from this process appear to be predominately uranium solids in the form of Clarkeite $[Na[(UO_2)O(OH)](H_2O)_{0-1}]$. Also note that uranium would be the limiting component in the final volume of repository waste and will provide a basis for optimization of the proposed treatment process for dissolution of aluminum at the Hanford Waste Treatment Plant.

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