# Gibbsite Solubility in Hanford Nuclear Waste Approached from above and below Saturation

Jacob G. Reynolds,* Jacob K. McCoskey, and Daniel L. Herting

Washington River Protection Solutions, LLC, P.O. Box 850, Richland, Washington 99352, United States

**S** *Supporting Information*

**ABSTRACT:** Liquid Hanford nuclear wastes are highly concentrated caustic aqueous electrolyte solutions. They contain elevated dissolved aluminum concentrations compared to simple $NaOH_{(aq)}$ solutions in equilibrium with gibbsite [$\gamma$-$Al(OH)_3$]. The reason for this elevated solubility has been debated for years, with slow gibbsite precipitation kinetics or various unverified thermodynamic factors being historically offered as explanations. The present study determines whether there is a kinetic or thermodynamic explanation. Here, dissolved aluminum in real tank waste was equilibrated with excess gibbsite, approached from both above and below saturation at 40 °C. In both cases, the samples equilibrated to an aluminum concentration up to four times higher than in pure $NaOH_{(aq)}$ solutions of the same hydroxide concentration. However, in one case, when all of the gibbsite dissolved during heating, no measurable precipitation was observed from the supersaturation direction when gibbsite seed was unavailable for nucleation. These results indicate that there is a real (and, as of yet, unknown) thermodynamic effect that accounts for the elevated solubility of aluminum exhibited by the waste. There is also a kinetic effect superimposed under some conditions.
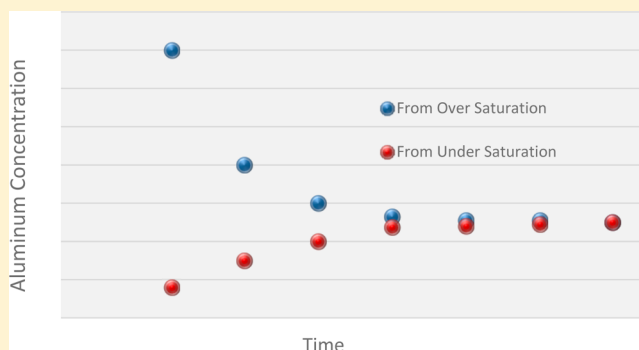
## 1. INTRODUCTION

The Hanford site, near Richland, WA, (U.S.A.), has about 55 million gallons of nuclear waste left over from plutonium production. The waste came from the processing of spent nuclear fuel for plutonium production. Aluminum(III) is one of the most prevalent constituents in nuclear waste at the Hanford Site. The Tank Waste Inventory Network System (TWINS) database maintained by the Hanford site tank farm operating contractor indicates that there is approximately $8.64 \times 10^6$ kg of aluminum in the Hanford waste tanks. The aluminum in the waste came from many different sources: (1) About 50% of it was used to increase the ionic strength in separation processes. (2) About 45% of the aluminum was a component of fuel cladding. (3) About 5% of the aluminum was a complexant added to some processes to prevent steel corrosion by the fluoride ion. The waste is now stored at both sites in the form of sludges, saltcakes, and highly concentrated electrolyte solutions (supernatant liquid).[1,2] Aluminum is commonly found in all three of these waste phases at greater than one wt % concentrations. Uranium is the most prevalent radio-nuclide on a mass basis (estimated to be about $6.48 \times 10^5$ kg by the TWINS database), but there is more than 13 times more aluminum in the waste than uranium. Thus, even though aluminum is not radioactive, the sheer quantity of aluminum in the waste may drive waste behavior. There is also a large amount of aluminum-bearing nuclear waste at the Savannah River site in South Carolina. Staff at the Hanford and Savannah River sites are planning and employing separation processes for

waste treatment, and the fate of aluminum in these processes is expected to depend on aluminum solubility in the waste.

The pH of most Hanford waste is greater than 13, and it is common to have dissolved hydroxide concentrations greater than 1 molar. At these high pH values, dissolved aluminum is predominantly in the form of the aluminate ion, $Al(OH)_4^-$, which has been directly identified in Hanford waste.[3,4] Sodium can form a contact ion-pair with aluminate.[3,5] Aluminate can dimerize in concentrated electrolyte solutions,[6] and the aluminate dimer has been observed in Hanford waste simulants.[7] The exact chemical formula for the dimer is still ambiguous, but past research has assumed it has the formula $(OH)_3Al-O-Al(OH)_3^{2-}$.[3] The aluminate dimer is reportedly a trace aluminum species relative to the monomer in concentrated NaOH solutions.[3] Reynolds and Reynolds[8] have hypothesized that the dimer would be more important in Hanford waste than in concentrated NaOH, but would still be less prevalent than the monomeric aluminate ion.

Some solid phases containing aluminum that have been identified in the waste are gibbsite ($Al(OH)_3$), boehmite ($AlOOH$), Dawsonite ($NaAl(OH)_2CO_3$), and sodium alumi-nosilicates.[9−13] Boehmite is widespread in tanks at both Hanford and Savannah River.[10,11,14] Boehmite dissolves and

precipitates at high temperatures, but both precipitation and dissolution kinetics are extremely slow below the highest current tank temperature of 45 °C.[15,16] Consequently, boehmite would not be expected to equilibrate with the liquid phase of the tanks over a reasonable time frame at Hanford. Dawsonite has also been found in some tanks at Hanford, and may equilibrate rapidly with the waste,[12] but it is not clear how widespread the phase is across all of the tanks at the Hanford and Savannah River sites. Scanning Electron Microscopy can often locate sodium aluminosilicates in waste tank solid samples,[9,12,13] but the concentration of silicon in most tanks is small. Consequently, even if all of the silica in the waste went to sodium aluminosilicate precipitation, little of the aluminum inventory would partition into this phase.[12] Gibbsite, however, is widespread in Hanford waste,[10,17] and the dissolution and precipitation kinetics of gibbsite are much faster at ambient temperatures than those of boehmite in $NaOH_{(aq)}$.

Staff at the Hanford site has long assumed that the liquid phase aluminum would equilibrate with gibbsite at ambient tank temperatures per the reaction in eq 1.

$$Al(OH)_{3(s)} + OH^-_{(aq)} \leftrightarrow Al(OH)^-_{4(aq)} \tag{1}$$
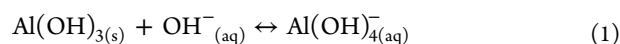
The apparent solubility of aluminum in Hanford waste, as indicated by waste assays, is considerably higher than is expected based on the current understanding of gibbsite solubility in high pH systems.[8,18,19] Reynolds[18] found that the dissolved aluminum concentration in Hanford waste is between 8 and 14 times higher than simple $NaOH_{(aq)}$ solutions of the same dissolved hydroxide concentration in equilibrium with gibbsite. Reynolds and Reynolds gave several alternative hypotheses for this apparent enhanced solubility.[8] One of those hypotheses is that gibbsite may just be very slow to precipitate. While aluminum can take a long time to reach equilibrium with gibbsite from the supersaturation direction at low temperatures,[20−22] Reynolds[18] noted that some Hanford tank liquids were still apparently supersaturated even after sitting stagnant for more than 20 years. Twenty years is an excessively long time to reach equilibrium in simple $NaOH_{(aq)}$ solutions, but conceivably could be a realistic time frame in Hanford waste that is known to have gibbsite crystallization inhibitors such as organics.[23−28] The alternative to the kinetic explanation would be some thermodynamic factor that is still not understood.[8]

Much of the waste in the tanks would be expected to have approached gibbsite solubility from the super saturation direction because some of the waste was processed through the "Partial Neutralization Campaigns" that added $HNO_3$ to the waste in order to precipitate $NaNO_3$,[29,30] and much of the original waste was created by neutralizing acidic streams using NaOH in the plutonium separation plants. One of the more plausible kinetic explanations for the elevated aluminum concentrations in the waste is that $CO_2$ is being absorbed by the waste from the atmosphere and also generated from the degradation of organics,[31−33] which is slowly acidifying the waste. The rate of waste acidification from $CO_2$ only has to be slightly faster than the rate of gibbsite precipitation for the waste to be chronically supersaturated with gibbsite. Nonetheless, when evaporator campaigns with elevated NaOH was mixed with waste that had gibbsite in it, that individual tank would be expected to be undersaturated with gibbsite rather than over saturated, yet all waste was supersaturated.[18] Thus, we cannot be assured that all of the waste would have come

from the supersaturation direction without a detailed historical analysis.

Reynolds and Reynolds evaluated historic gibbsite solubility data for Hanford waste and waste simulants.[8] They noted that the solubility experiments conducted to date have only been conducted from the supersaturation direction, and thus may be biased by slow precipitation kinetics. No prior work has equilibrated a sample of actual Hanford waste with gibbsite from both above and below saturation to determine if the liquid phase concentration approaches the same value. Such an experiment would determine whether the apparent high dissolved aluminum concentration in the waste is truly soluble or is just a result of slow precipitation kinetics. The present study undertakes that experiment.

The question, "is the aluminum concentration controlled by kinetics or thermodynamics?", has practical considerations. If the waste is chronically supersaturated as it sits, perturbation of the waste may cause unwanted precipitation. Potential places where aluminum could precipitate would be areas where the nucleation surfaces are very different than in the waste tanks, such as inside ion-exchange columns or inside the pores of filters. Indeed, aluminum precipitation has been implicated in the fouling of ion-exchange columns at both Hanford and the Savannah River sites.[34−36]

At the Hanford site, current waste treatment plans include leaching both gibbsite and boehmite from the waste by adding NaOH and raising the temperature.[37,38] The Savannah River Site has already begun leaching aluminum with NaOH by raising the temperature.[39−41] At the Hanford site, about 25% of all of the sodium vitrified as waste glass is sodium used to leach aluminum and keep it soluble after it has cooled to ambient temperatures.[42] If the aluminum were found to be more soluble in tank waste than in simple NaOH solutions, the amount of NaOH added could be minimized.

In addition to high-level waste processing, the solubility of aluminum may be important to contaminant transport in soils at Hanford. Historic tank leaks at Hanford have resulted in the discharge of radioactive waste to soils underlying the tanks.[43] Whatever factors are influencing the solubility of aluminum in tank waste may also be important to soil where this waste has leaked. Aluminate reportedly impacts the fate of radionuclides in soils contaminated with Hanford tank waste.[44−48] Thus, understanding the factors that control aluminate concentration in Hanford waste may ultimately increase our understanding of the fate and transport of contaminants in the Hanford vadose zone.

## 2. EXPERIMENTAL METHODS

The samples used in this experiment came from Hanford tank 241-AN-105 (AN-105), taken using a core sampling method described in by the American Society for Testing Materials.[49] Solids in this tank are saltcake created by evaporating concentrated waste electrolyte solutions in the Hanford evaporator in the 1980s.[50] Both salt and overlying supernatant solution from this tank were used in the present experiments. Commercial gibbsite (Almatis, C33) was added to the samples in these experiments to ensure that there is sufficient aluminum present to equilibrate with gibbsite. This tank was selected because calculations using the commercial thermodynamic software Environmental Simulation Program (Version 8.3) by OLI Incorporated (Morristown, N.J., U.S.A.) indicate that this sample is under saturated with gibbsite at the target temperature. This undersaturated waste sample could be used

to approach equilibrium from below saturation. The sample is likely below saturation because there is no more gibbsite in the tank left to dissolve.

In order to determine the impact of waste solids on aluminum, some samples used only the supernatant liquid and other experiments used both supernatant liquid and the saltcake (Table 1). The saltcake portion of the sample

**Table 1. Experimental Slurry Composition**

| Experiment | Tank AN-105 Supernate (g) | Tank AN-105 Saltcake (g) | Almatis C33 Gibbsite (g) | Wt% Solids in saltcake fraction |
|---|---|---|---|---|
| 1 (Top Down, no native solids) | 97.26 | 0.00 | 24.23 | - |
| 2 (Bottom up, no native solids) | 84.64 | 0.00 | 21.52 | - |
| 3 (Top Down, with native solids) | 91.95 | 16.49 | 11.50 | 71.3% |
| 4 (Bottom Up, with native solids) | 91.24 | 16.57 | 11.56 | 71.3% |

contained entrained interstitial liquid, so Table 1 reports both the mass of saltcake used in each experiment and the mass of solids in the saltcake determined by a water content measurement. In order to simplify communication, the samples equilibrated from below saturation are here denoted "Bottom up" samples and samples equilibrated from above saturation are denoted "Top Down" experiments. Similarly, samples having actual solids from tank AN-105 are denoted as having "native solids" and samples without these solids are referred to as having no native solids.

The experiments were carried out in a custom fabricated reactor made from 250 mL polymethylpentene jars. A sample port made of a 1/2 in. perfluoroalkoxy alkane (PFA) fitting and 1/2 in. PFA rod was installed on the lid of the jar for ease of sampling. An 18 in. long, 1/8th inch OD PFA tube with glass wool in the outer end was attached to the lid through a PFA fitting to act as refluxer. The refluxer was installed to decrease vapor losses and ensure the contents of the reactor did not pressurize during heating of the solution.

The reactors were heated and stirred by means of a hot/stir plate. The reactor was encased in an aluminum metal block so the reactor did not come into direct contact with the hot plate and to moderate hot plate induced temperature cycling. The temperature was regulated to ±1 °C by the hot plate temperature controller and checked regularly with a NIST-traceable thermometer. A three inch long by 3/8 in. diameter Teflon coated stir bar was used to stir the slurry.

Experiments 1 through 4 (see Table 1) were equilibrated at 40 °C, to match the experimental temperature employed by Russell et al.[51] for gibbsite solubility in $NaOH_{(aq)}$ solutions. This is also near temperature (45 °C) where aluminum was observed to plug a lab-scale ion exchange column.[35] Two samples contained only AN-105 supernatant solution and Almatis gibbsite, one where equilibrium was approached from below saturation (bottom-up) and one where equilibrium was approached from above saturation (top-down). Two other samples contained tank AN-105 supernatant solution, native solids, and gibbsite, approaching equilibrium from both directions (top-down and bottom-up). The samples for the bottom-up experiments were heated up to 40 °C from the sample storage temperature of 29 °C. The top-down

experiments were heated to 85 °C for 4−6 h to ensure that they were supersaturated with aluminum before they were cooled to 40 °C. The dissolution temperature of 85 °C was chosen because this is the solids leaching temperature target anticipated at the Hanford Waste Treatment and Immobilization Plant (WTP). The bottom-up experiments were incubated for 45 days. The samples in experiment 1 were incubated for 21 days after which experimental difficulties prevented additional incubation. Inspecting the data of this sample showed that it had essentially reached equilibrium at 21 days (see Results section). The top-down experiments with native AN-105 solids were incubated 60 days.

All preparations were sampled intermittently over the incubation period. Supernatant liquid was sampled from the reactors at temperature using a disposable PFA pipet and the slurry delivered into a 5 mL syringe filter to remove the solids. The filtered solution was delivered from the syringe filter into a 5 mL polycarbonate test tube. Three 1 mL aliquots of sample were then delivered using a volumetric pipet to a 20 mL polypropylene sample jar containing 3 mL of 5 molar NaOH to stabilize the solution and prevent solids from precipitating from solution. A 1000 μL Eppendorf Reference volumetric pipet was calibrated during each sampling event using the three aliquots of 5 molar NaOH solution. Also, blanks containing six 1 mL aliquots of NaOH were delivered as samples for analysis. The sample and NaOH were delivered to the sample jar as 1 mL aliquots to define the density of sample and define the quality attributes of the method, respectively.

The initial sludge and supernatant liquid samples were analyzed for the chemical and physical constituents listed in Table 2 by Advanced Technologies and Laboratories Interna-

**Table 2. Analysis Techniques Conducted by Advanced Technologies and Laboratories International, Inc.**

| Method | Analytes |
|---|---|
| Inductively Coupled Plasma (ICP) atomic emissions spectroscopy | Al, Cr, P, S, Na |
| Ion Chromatography (IC) | $NO_3^-$, $NO_2^-$, $SO_4^{2-}$, $PO_4^{3-}$, $Cl^-$, $F^-$, $Br^-$, $HCOO^-$, $C_2H_3O_3^-$, $C_2H_3O_2^-$, $C_2O_4^{2-}$ |
| Silver catalyzed persulfate oxidation in acidified solution with Coulombic detection | Total organic carbon, total inorganic carbon |
| Titration | $OH^-$ |
| Thermogravimetric Analysis | $H_2O$ |
| Density (pipet a known volume into a flask on a balance) | Density |

tional, Inc. The solids were analyzed by Inductively Coupled Plasma Atomic Emissions Spectroscopy (ICP) after undergoing acid digestion in nitric acid and peroxide solution. Hydroxide was measured by titration, by difference between measured and hydroxide added for sample preservation, after competing species that consume acid were precipitated with barium chloride. Aluminum, hydroxide, water content and density were measured in all samples taken. The solids were probed for gibbsite by X-ray Diffraction (XRD). The samples for XRD were prepared by centrifuging the solids, evaporating the liquid from the centrifuged solids, and placing the solids on zero-background quartz slides.

Bloom and Weaver indicated that the solubility of gibbsite was sensitive to small quantities of amorphous gel impurities at pH 3.7.[52] The solubility of gibbsite is extremely small at pH 3.7 relative to Hanford waste. Any amorphous gel impurity (if

present) in our gibbsite would likely have been completely dissolved and thus would not have impacted the results in our experiments. To be sure that our results were not impacted by a potential amorphous gel impurity, however, we equilibrated samples of the gibbsite used in this study in simple $NaOH_{(aq)}$ solutions at 40 °C. The results of these could then be compared to gibbsite solubility measurements reported by Russell et al.[51] and the real waste samples.

## 3. RESULTS

The major components in the liquid phase at the start of the experiments are sodium, nitrate, nitrite, hydroxide, aluminum (presumably as aluminate), chloride, inorganic carbon (presumably as carbonate), and sulfate (Table 3). This list of major

**Table 3. Supernatant Liquid Chemical Analysis (units of molality unless otherwise specified)**

| Species/Result | Concentration |
| --- | --- |
| Density (g/mL) | 1.45 |
| Wt% $H_2O$ | 45.4 |
| Aluminum | 1.24 |
| Chromium | 0.006 |
| Potassium | 0.30 |
| Phosphorus | 0.018 |
| Sodium | 17.48 |
| Sulfur | 0.054 |
| Fluoride | 0.015 |
| Glycolate | 0.017 |
| Acetate | 0.049 |
| Formate | 0.064 |
| Chloride | 0.510 |
| Nitrite | 4.58 |
| Sulfate | 0.019 |
| Nitrate | 4.08 |
| Phosphate | 0.017 |
| Inorganic carbon as $CO_3$ | 0.35 |
| Total Organic Carbon | 0.34 |
| Free Hydroxide | 6.06 |

constituents is typical of all Hanford liquid waste, though the relative and absolute concentration of these constituents varies widely among the waste tanks.[53]

Figure 1 shows the concentrations of aluminum and hydroxide in the samples as a function time for the samples without native solids. The bottom-up experiments reached an
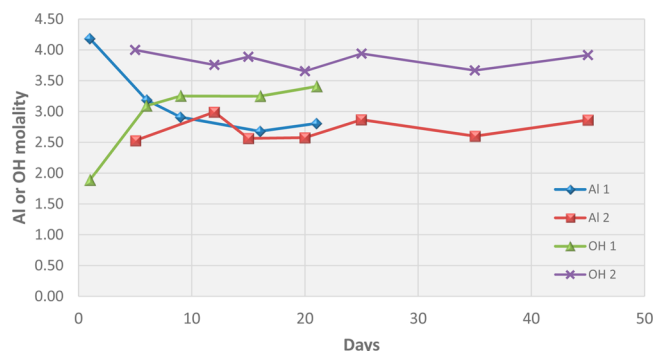


**Figure 1.** Aluminum and free hydroxide molality as a function of time in the AN-105 samples with only supernatant liquid and added gibbsite. [Experiment 1, top down; Experiment 2, bottom up.]

approximate steady-state concentration by the time the first sample was taken after 8 days. Aluminum precipitated in the top down experiments for the first 12 days as is evident by the drop in aluminum concentration and rise in hydroxide concentration (Figure 1). The rise in hydroxide concentration was approximately equal to the drop in the aluminum concentration, as expected from eq 1, providing evidence that aluminum hydroxide was precipitating in this sample. The aluminum concentration approached the same value from both above and below saturation after about 12 days. The hydroxide concentration also reached a near steady state concentration in both samples over this same time period, but the absolute concentration of hydroxide was slightly lower in the samples equilibrated from above saturation. From Figure 1 it is clear that the samples approached the same concentration both from above and from below saturation, a conclusion that will be discussed in more detail later.

Figure 1 clearly shows that the precipitation of gibbsite was slower than the dissolution, taking 12 days to approach equilibrium rather than about 5 days from undersaturation. Nonetheless, this does not account for the elevated aluminum concentrations observed in tanks stagnant for months to years described in reference.[18]

Figure 2 shows the change in aluminum and hydroxide concentration with time in samples that had native AN-105
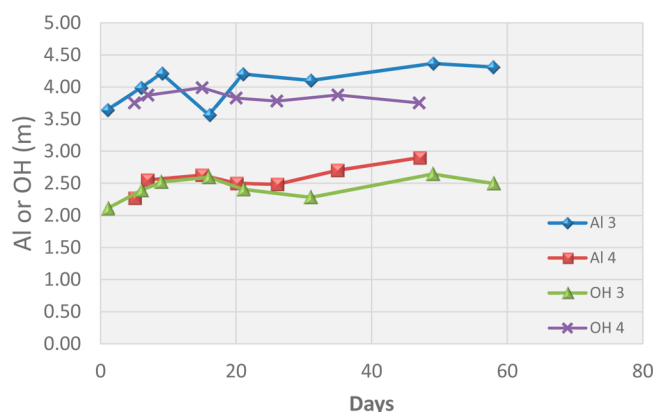


**Figure 2.** Aluminum and free hydroxide molality as a function of time in samples with added gibbsite and tank AN-105 solids. [Experiment 3, top down; Experiment 4, bottom up.]

solids. As seen in Figure 2, the bottom-up experiments with native solids reached an apparent steady state aluminum concentration within 12 days. The aluminum and hydroxide concentrations of this bottom up experiment were nearly the same as the samples without native solids displayed in Figure 1. The aluminum concentration of the top-down experiment was much higher than the bottom up, and the hydroxide concentration was much lower at the end of the experiment. Indeed, the top-down experiments with native AN-105 solids showed no evidence of aluminum precipitation at all when the samples had cooled to 40 °C for at least 60 days and did not approach the concentration found in the bottom-up experiments. This indicates that gibbsite was kinetically slow to precipitate in this sample. This result clearly shows that some conditions can prevent aluminum precipitation for extended periods, and therefore, slow kinetics could conceivably account for the elevated aluminum concentration in some tank wastes. Nonetheless, the kinetics of aluminum precipitation was relatively fast in experiment 1.

**Table 4. Average Concentration of Aluminum and Hydroxide When Samples Reached Steady State**

| Experiment Number | Samples Averaged (Days) | Statistic | $Al(OH)_4^-$ (m) | $OH^-$ (m) | $\rho$ (g/mL) | Wt% $H_2O$ |
|---|---|---|---|---|---|---|
| 1 (top down, no native solids) | 9, 16, 21 | Mean | 2.8 | 3.3 | 1.45 | 48.8 |
| | | Standard Deviation | 0.35 | 0.27 | 0.013 | 0.38 |
| 2 (bottom up, no native solids) | 12−45 | Mean | 2.7 | 3.8 | 1.45 | 48.66 |
| | | Standard Deviation | 0.56 | 0.38 | 0.05 | 2.48 |
| 3 (top down, native solids) | 9−58[a] | Mean | 4.2 | 2.5 | 1.53 | 44.9 |
| | | Standard Deviation | 0.31 | 0.39 | 0.08 | 3.4 |
| 4 (bottom up, native solids) | 15−47 | Mean | 2.6 | 3.8 | 1.49 | 47.7 |
| | | Standard Deviation | 0.51 | 0.28 | 0.08 | 1.9 |

[a]The aluminate data from day 16 was omitted from the average.

The XRD analysis identified gibbsite in the solids of experiments 1, 2 and 4, but no gibbsite was found in experiment 3. This is consistent with the observation in Figure 2 that aluminum did not reprecipitate appreciably in experiment 3. Thus, the XRD and solution phase data independently indicate that aluminum precipitation was inhibited in experiment 3, but gibbsite was the solid-phase aluminum species in all other treatments. The dominant solid in the native solids in experiment 3 was thermonatrite ($Na_2CO_3 \cdot H_2O$).

The aluminum and hydroxide concentrations for the sample times that reached a steady state value were averaged so that an apparent equilibrium concentration could be estimated. Table 4 lists the time range that the authors used to calculate these averages (which can be compared to the plots in Figures 1 and 2), as well as the density ($\rho$) and water content measurements used to convert to molality units.

A statistical analysis of the mean aluminum and hydroxide concentrations was conducted to determine if the calculated means agree to the 99% confidence interval. A manual inspection of the mean aluminum concentration of experiments 1, 2, and 4 demonstrate that the values are similar. The statistical analysis confirms that the mean aluminum concentrations for these three experiments agree with a confidence greater than 99% (see Table 5). In other words, the presence or

**Table 5. F-Test and t-Test Results for AN-105 Experiments**

| Al | F-test | t test | $\alpha$ | Confidence |
|---|---|---|---|---|
| Exp. 1-1 vs Exp. 1-2 | Equal Variance | Equal Means | 0.01 | >99% |
| Exp. 1-1 vs Exp. 1-3 | Equal Variance | Unequal Means | 0.99 | - |
| Exp. 1-1 vs Exp. 1-4 | Equal Variance | Equal Means | 0.01 | >99% |
| Exp. 1-2 vs Exp. 1-3 | Equal Variance | Unequal Means | 0.99 | - |
| Exp. 1-2 vs Exp. 1-4 | Equal Variance | Equal Means | 0.01 | >99% |
| Exp. 1-3 vs Exp. 1-4 | Equal Variance | Unequal Means | 0.99 | - |
| **OH** | **F-test** | **t test** | **$\alpha$** | **Confidence** |
| Exp. 1-1 vs Exp. 1-2 | Equal Variance | Unequal Means | 0.99 | - |
| Exp. 1-1 vs Exp. 1-3 | Equal Variance | Unequal Means | 0.99 | - |
| Exp. 1-1 vs Exp. 1-4 | Equal Variance | Unequal Means | 0.99 | - |
| Exp. 1-2 vs Exp. 1-3 | Equal Variance | Unequal Means | 0.99 | - |
| Exp. 1-2 vs Exp. 1-4 | Equal Variance | Equal Means | 0.01 | >99% |
| Exp. 1-3 vs k Exp. 1-4 | Equal Variance | Unequal Means | 0.99 | - |

absence of native solids did not impact the equilibrium concentration of aluminum in the bottom-up experiments. The outlier was experiment 3, which is the top down experiment with native solids. In this case, the aluminum concentration was nearly double the concentration of the other experiments. This is consistent with the graphical analysis in Figures 1 and 2.

The hydroxide concentrations at equilibrium between the four experiments were also evaluated. Experiments 2 and 4 were statistically equivalent at the 99% level. In both cases, equilibrium was approached from below the aluminum saturation point, but experiment 4 had native solids and experiment 2 did not have native solids. This indicates that both bottom-up experiments reached the same value regardless if native solids were present or not.

The top-down experiment # 1 did not have the same hydroxide concentration as the bottom up experiment at the 99% level, but the magnitude of the difference was not large. If just 0.2 more mols/kg of aluminum precipitated as gibbsite per eq 1 in experiment 1, the aluminum concentration would still have been within the standard deviation of experiments 2 and 4. The 0.2 mol/kg hydroxide created would have resulted in a hydroxide concentration in experiment 1 within the standard deviation of experiments 2 and 4. Therefore, experiment 1 likely did not fully reach equilibrium. Nonetheless, experiment 1 came close to meeting experiment 2, indicating that the true equilibrium concentration was near the ending value for experiments 1 and 2.

Lastly, it is determined here that the results are not being biased by the concern raised by Bloom and Weaver for experiments using synthetic gibbsite.[52] Namely, they found that gibbsite equilibrated with an amorphous gel impurity rather than the gibbsite itself in their sample at pH 3.7.[52] This was confirmed to not bias the results here by comparing the solubility of the synthetic gibbsite used here against the solubility of gibbsite reported by Russell et al.[51] in aqueous $NaOH$ solutions. The excellent agreement between the results of Russell et al.[51] and the data collected here (Figure 3) indicate that the gibbsite either did not have an amorphous gel impurity or did not equilibrate with it. If the gibbsite had equilibrated with an amorphous gel impurity rather than gibbsite, the solubility in $NaOH_{(aq)}$ would have been higher than that exhibited by the Russell et al. data.[51] Any gel impurity that may have been in the synthetic gibbsite used here would have likely been dissolved completely. The gibbsite solubility data in $NaOH_{(aq)}$ are tabulated in the Supporting Information for use by future modelers.

It is not reasonable that the bottom up samples equilibrated with a more soluble aluminum-bearing phase than gibbsite because a substantial fraction of the dissolved aluminum came
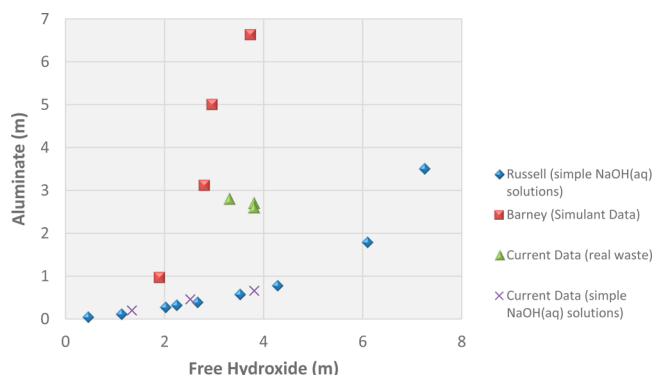
**Figure 3.** Gibbsite solubility at 40 °C in waste, simulant, and simple NaOH(aq) solutions.

from gibbsite dissolution, and it is not reasonable to believe that gibbsite would dissolve past its solubility point. It is certainly possible that a top down experiment could equilibrate with a more soluble phase and poise the dissolved aluminum concentration, but Figure 1 indicates that the top-down experiment came to approximately the same concentrations as the bottom up experiment, so we can rule out that they equilibrated with a species more soluble than gibbsite.

## 4. DISCUSSION

Given the close agreement among experiments 1, 2, and 4, these three samples were compared to historic data from Barney[54] for Hanford waste simulants and from Russell et al.[51] for simple NaOH(aq) solutions, all at 40 °C (Figure 3). Reynolds and Reynolds cover the history of the Barney data,[8] summarized here. Prior to Barney's work in 1976, the solubility of gibbsite in Hanford waste was assumed to be approximately the same as in simple NaOH(aq) solutions of the same free hydroxide concentration and temperature, such as the data from Russell et al.[51] In Barney's study, aluminum was considerably more soluble in simulated Hanford waste than in simple NaOH(aq) solutions. This is evident in Figure 3, which shows that Barney's[46] aluminum concentrations are approximately six times higher than Russell et al.'s.[51] This conclusion was surprising at the time of Barney's study, and the accuracy of that data has been debated since.[8] Many claimed that Barney had terminated his experiments too soon and his samples had simply not reached equilibrium (see Reynolds and Reynolds[8]). Nonetheless, there has been anecdotal evidence for a long time that actual tank waste also exhibits elevated dissolved aluminum concentrations. A recent systematic review of Hanford waste tank assays has confirmed this.[18] None of the previous Hanford waste solubility experiments had been equilibrated from below saturation, including Barney's.[8,54] Consequently, it was unknown whether the elevated aluminum concentrations that have been observed in previous studies are an artifact of slow precipitation kinetics.[8,18]

As is evident from Figure 3, the solubility of gibbsite exhibited by Hanford tank sample AN-105 was in-between Barney's[54] simulants and the NaOH(aq) solution data from Russell et al.[51] at the same hydroxide molality. The aluminum concentration is more than four times higher in the AN-105 supernatant samples studied here than in the simple NaOH(aq) solutions of the same hydroxide concentration. This is true even of the bottom-up experiments, and it is unlikely that the aluminum would have dissolved past the equilibrium point to reach a supersaturated state. Thus, Figure 3 is clear evidence

that there is indeed a thermodynamic effect that is at least partially responsible for the elevated concentration of aluminum in Hanford tank waste.

While Figure 3 clearly shows there is a thermodynamic effect that increases aluminum solubility in this Hanford waste sample relative to simple NaOH(aq) solutions, Figure 2 shows there is also a kinetic effect under some conditions. Thus, both kinetic effects and thermodynamic effects can play a role in the elevated concentrations of aluminum observed in Hanford waste. The present study was designed to determine whether the elevated aluminum concentration in Hanford waste was caused by a thermodynamic or kinetic effect, not to identify the mechanism of either one. Nonetheless, we can hypothesize that slow nucleation kinetics was a contributing factor to the slow precipitation kinetics observed in experiment 3. The differences between experiments 1 and 3 are the presence or absence of native solids in the samples and the total amount of gibbsite added to the system. In our experimental design, we kept the total amount of solids the same in experiments 1 and 3. Consequently, the quantity of gibbsite in experiment 1 equaled the quantity of gibbsite plus native solids in experiment 3, and the total amount of gibbsite was less in experiment 3 than experiment 1. When the samples in experiment 3 were heated to 85 °C, all of the gibbsite in the sample dissolved, whereas some of the gibbsite remained insoluble in experiment 1. Thus, gibbsite solids were available for nucleating more gibbsite when the samples were cooled back down to 40 °C in experiment 1. Gibbsite is known to be an excellent nucleation agent for precipitation of more gibbsite.[55] Thermonatrite ($Na_2CO_3 \cdot H_2O$) was the dominant solid in the saltcake identified by XRD in this study. Given the slow precipitation kinetics in experiment 3 relative to experiment 1, thermonatrite is evidently a poor nucleating agent for gibbsite. Sodium oxalate, hematite, and amorphous iron hydroxide are other solid phases that have been reported in other Hanford waste tanks and have also been reported to be good gibbsite nucleating agents, so there may be more gibbsite nucleation sites in other wastes that have these minerals.[12,19,56−59]

Modern aqueous solution modeling algorithms use interaction factors to account for interactions between components at high ionic strength that are in addition to the Debye−Hückel parameters that are only effective at low ionic strengths.[60−63] For instance, the popular Pitzer model uses cation−anion−anion and anion−anion interaction factors to account for anion−anion repulsion and the screening of this repulsion.[60,64] These factors for the Pitzer model, and many other solution models, must be calibrated by fitting the model to actual data. The enhanced solubility observed here is larger than the most common impact of these type of interactions,[60,65] but certainly not outside the realm of possibility. A Pitzer based model is under development for Hanford waste,[66−68] but the data is unavailable to calculate the anion-repulsion and screening effects of the anions in this complex nuclear waste mixture between aluminate and the common anions in Hanford nuclear waste. Thus, future refinements of the model for the aluminate ion will await new data.

The present study observed both kinetically controlled and thermodynamically controlled elevated aluminum concentrations in Hanford waste from one tank at Hanford. The waste electrolyte composition at both the Hanford and Savannah River sites is extremely variable.[53] Consequently, this study cannot determine the extent to which thermodynamic factors or slow kinetics account for the high concentrations of

aluminum in other individual tanks. What this study shows for certain, however, is that a thermodynamic effect is present in at least one Hanford waste that is not present in simple $NaOH_{(aq)}$ solutions. Earlier reports provide potential thermodynamic factors that may be contributing to the large apparent solubility of gibbsite.[8,18] Once this thermodynamic effect is understood and quantified in the form of a model, it may be easier to determine which tanks and to what extent slow precipitation kinetics accounts for the elevated aluminum concentrations. Such a modeling approach may more easily determine gibbsite solubility in other tanks than the labor intensive experiments employed here. Reynolds[18] showed that every Hanford tank investigated with a sodium molarity greater than two had elevated aluminum concentrations. Consequently, the kinetic and thermodynamic factors responsible for the elevated aluminum solubility may be widespread across the tanks, despite the large variability in waste composition.

## 5. CONCLUSION

This study answers the longstanding question about the anomalously high apparent solubility in Hanford nuclear waste, "Is this a thermodynamic effect, or is this just a result of extremely slow gibbsite precipitation kinetics?", which had never been answered before. The present study answers this question by equilibrating a sample of waste with gibbsite while approaching the same concentration from both above and below saturation. The results showed that the solubility of gibbsite was between 3 and 4 times larger than in simple NaOH(aq) solutions. Nonetheless, there was slow gibbsite precipitation kinetics in a sample with no gibbsite seed crystals. These results will allow process engineers to evaluate the amount of NaOH that must be added to prevent aluminum precipitation from the waste during processing. This is particularly important because any sodium added as NaOH must subsequently be treated and disposed of as part of the nuclear waste.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b00743.

Table of the solubility of gibbsite in $NaOH_{(aq)}$ (PDF)

## ■ AUTHOR INFORMATION

**Corresponding Author**
*E-mail: jacob_g_reynolds@rl.gov.

**Notes**

The authors declare no competing financial interest.

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