A Modern Interpretation of the Barney Diagram for Aluminum Solubility in Tank Waste – 10075

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ABSTRACT

Experimental and modeling studies of aluminum solubility in Hanford tank waste have been developed and refined for many years in efforts to resolve new issues or develop waste treatment flowsheets. The earliest of these studies was conducted by G. Scott Barney, who performed solubility studies in highly concentrated electrolyte solutions to support evaporator campaign flowsheets in the 1970's. The "Barney Diagram", a term still widely used at Hanford today, suggested gibbsite (γ-Al(OH)$_3$) was much more soluble in tank waste than in simple sodium hydroxide solutions. These results, which were highly surprising at the time, continue to be applied to new situations where aluminum solubility in tank waste is of interest. Here, we review the history and provide a modern explanation for the large gibbsite solubility observed by Barney, an explanation based on basic research that has been performed and published in the last 30 years. This explanation has both thermodynamic and kinetic aspects. Thermodynamically, saturated salt solutions stabilize soluble aluminate species that are minor components in simple sodium hydroxide solutions. These species are the aluminate dimer and the sodium-aluminate ion-pair. Ion-pairs must be present in the Barney simulants because calculations showed that there was insufficient space between the highly concentrated ions for a water molecule. Thus, most of the ions in the simulants have to be ion-paired. Kinetics likely played a role as well. The simulants were incubated for four to seven days, and more recent data indicate that this was unlikely sufficient time to achieve equilibrium from supersaturation. These results allow us to evaluate applications of the Barney results to current and future tank waste issues or flowsheets.

INTRODUCTION

The solubility of aluminum in Hanford tank waste liquor is of current interest. Aluminum dissolution is a key to the removal of heels at the bottom of tanks, aluminum is planned to be leached from sludge at the Hanford Waste Treatment and Immobilization Plant, and there is a general need to understand the amount of solids in waste streams. Consequently, models are needed for aluminum solubility in tank waste. An obvious approach for understanding current issues with aluminum solubility is to look at historic data and modeling methods.

The present paper is the first of a two-part series on the history of aluminum solubility modeling in Hanford waste. This paper covers the early study by Barney [1], work still widely used today. This paper not only covers the history of that study but also provides our best modern interpretation of Barney's observations, observation that were highly surprising at the time. This early study provided a basis for subsequent modeling studies that will be covered in part two of this series.

ALUMINUM CHEMISTRY OVERVIEW

Early (pre 1970's) work reported in the literature on aluminum solubility in highly caustic solutions was primarily performed by the alumina refining industry. Alumina refineries separate aluminum from ores by dissolving it with sodium hydroxide. The aluminum solubility data in simple sodium hydroxide solutions was the only data available at high-pH before the Barney [1] study, so that data provided the frame of reference for Hanford workers at the time. In 1989, Apps and Others [2] compiled all of the aluminum solubility data available for these simple systems. Those studies showed that the aluminum solubility in sodium hydroxide solutions depends on the mineral form of aluminum.

Many aluminum containing minerals have been identified in Hanford waste, but Gimpel and Reynolds [3] listed gibbsite (γ-Al(OH)$_3$) and boehmite (γ-AlOOH) as the most prevalent. Both the precipitation and dissolution kinetics of boehmite are extremely slow at current tank temperatures [4, 5], so boehmite is not expected to effectively contribute to the solubility of aluminum observed in the waste under current conditions. Boehmite is believed to have formed in the tanks at a time when they were allowed to self-boil [6, 7]. Gibbsite is expected to be the most important species controlling the solubility of aluminum in most tanks over the time and temperature interval relevant to waste treatment. Sodium aluminate solubility was of much interest in the 1970's because the tank farm wanted to know how much they could evaporate waste without precipitating sodium aluminate. Sodium aluminate is highly soluble, except at extremely high sodium concentrations [1, 8].

The dominant aluminum species in high-pH liquids is believed to be the aluminate ion Al(OH)$_4^-$ [9]. Before the advent of solution spectroscopic techniques, aluminate was believed to have the stoichiometry AlO$_2^-$, but this stoichiometry has since been disproven [9]. Nonetheless, for historical reasons, aluminate in solution is still frequently referred to as AlO$_2^-$, and this terminology is frequently used in the nuclear waste literature. In addition to Al(OH)$_4^-$, other species of dissolved aluminum have been identified in caustic aluminate solutions but have assumed to have negligible concentrations [9, 10]. As will be shown later, these minor species may be more significant in the Barney studies and may play a role in the enhanced solubility of gibbsite in tank waste.

The reaction between hydroxide, aluminate, and gibbsite is:

$$Al(OH)_{3\,(s)} + OH^-_{(aq)} \leftrightarrow Al(OH)^-_{4\,(aq)} \tag{Eq. 1}$$

The equilibrium expression for the reaction in Equation 1 is

$$K = \frac{a_{Al(OH)_4^-}}{a_{OH^-}} \qquad \text{(Eq. 2)}$$

where K is the equilibrium constant and the 'a' in Equation 2 represents the activity of the species in the subscript. The activities of the ions, in turn, are functions of the concentration and activity coefficient of the species:

$$a_i = C_i \lambda_i \qquad \text{(Eq. 3)}$$

where C_i is the concentration of ion 'i' and λ is the activity coefficient. The activity coefficient is a complex function of the concentration and composition of all of the ions in solution, a function that is not the same for all ions [11]. Nonetheless, a number of models for calculating activity coefficients appear to accurately reflect data for the simple sodium hydroxide-sodium aluminate-water system [12, 13].

Similar to the reaction above, the reaction to form sodium aluminate solid can be written:

$$Na^+_{(aq)} + Al(OH)^-_{4(aq)} \leftrightarrow NaAl(OH)_{4(s)} \qquad \text{(Eq. 4)}$$

With accompanying equilibrium expression

$$K = \frac{\left(a_{Na^+}\right)\left(a_{Al(OH)_4^-}\right)}{1} \qquad \text{(Eq. 5)}$$

One observation that can be deduced from the reactions in Equations 1 and 4 is that adding free hydroxide encourages gibbsite to dissolve and adding sodium encourages sodium aluminate to precipitate. Thus, when sodium hydroxide is added to a solution intermixed with solid gibbsite, the gibbsite dissolves. If enough sodium hydroxide is added, however, that aluminum re-precipitates as sodium aluminate. As will be shown in the next section, there is an optimal sodium hydroxide concentration where the maximum quantity of aluminum is dissolved while avoiding sodium aluminate precipitation.

THE BARNEY DATA AND DIAGRAM

During the 1970's and early 1980's, the Hanford Tank Farm was using an evaporator/crystallizer to produce saltcakes to maximize tank space [14]. They were adding nitric acid to the evaporators in the "partial neutralization" evaporator campaigns in order to convert sodium hydroxide to sodium nitrate [15]. Sodium nitrate was easier to crystallize than sodium hydroxide [15]. Aluminum solubility was important to these campaigns because they wanted to limit the quantity of nitric acid added to avoid

aluminum precipitation. Thus, Barney [1] performed a solubility study to support the development of the evaporator flowsheet [16].

The saltcakes produced by the evaporator were to be saturated with sodium nitrate, sodium carbonate, and other salts. Therefore, Barney [1] performed his aluminum solubility studies in simulated supernatants that were simultaneously saturated with several salts. Barney [1] evaluated aluminum solubility as a function of temperature and the amount of sodium hydroxide added. Barney's data is shown in Tables I and II.

Table I. Simulant Compositions Studied by Barney [1].

Sample Number[a]	NaOH (M)	NaAl(OH)$_4$ (M)	NaNO$_3$ (M)	NaNO$_2$ (M)	Na$_2$CO$_3$ (M)
1	15.9	0.17	0.52	0.72	0.023
1	17.5	0.26	0.34	0.82	0.021
1	17.2	0.17	0.34	0.94	0.019
1	26.3	0.17	0.27	0.8	0.037
6A	9.1	1	1.6	1.47	0.13
6A	7.68	1.32	2.1	2.4	0.31
6A	7.2	1.24	2.7	2.83	0.13
6A	7.66	1.4	2.7	3.08	0.2
2A	4.61	2.6	2	2.55	0.12
2A	4.41	2.67	2.5	2.95	0.08
2A	unreported	2.47	3.2	3.53	0.12
2A	4.45	2.69	2.5	2.98	0.08
3A	2.07	3.77	2.6	2.85	0.22
3A	2.14	3.81	2.7	2.91	0.17
3A	2.38	3.89	2.7	2.66	0.08
3A	2.48	3.77	2.5	2.86	0.25
3.5 A	unreported	2.24	2.8	3.38	0.21
3.5 A	1.71	2.91	3.2	4.01	0.15
3.5 A	1.2	3.24	3.6	4.09	0.14
3.5 A	1.49	3.17	3	3.67	0.13
4A	1.7	1.94	3.1	3.31	0.25
4A	1.79	2	3.3	4.2	0.18
4A	1.46	2.42	3.4	3.8	0.31
4A	1.55	2.42	3	3.99	0.36
5A	1.26	0.7	3.9	4.19	0.27
5A	1.2	0.62	4.2	5.36	0.21
5A	0.92	0.72	4	4.66	0.32
5A	0.83	0.74	3.8	4.57	0.28

a.   Samples with the same name are at different temperatures, See Table II.

Table II. Properties of the Barney [1] Simulants.

Sample Number	Temperature in Celsius	Vapor Pressure (mm Hg)	Water Activity	Density (g/mL)
1	20	2.5	0.143	1.51
1	40	2.4	0.043	1.59
1	60	7.1	0.048	1.61
1	80	9.9	0.028	1.68
6A	20	4.9	0.280	1.49
6A	40	14.1	0.255	1.51
6A	60	38.9	0.260	1.55
6A	80	86.4	0.243	1.46
2A	20	6.4	0.366	1.55
2A	40	17.7	0.320	1.58
2A	60	48.6	0.325	1.59
2A	80	127	0.358	1.57
3A	20	8.1	0.463	1.55
3A	40	21.9	0.396	1.56
3A	60	59.8	0.400	1.55
3A	80	140	0.394	1.54
3.5 A	20	10.8	0.617	1.53
3.5 A	40	22.3	0.403	1.56
3.5 A	60	57.7	0.386	1.57
3.5 A	80	165	0.465	1.56
4A	20	10.3	0.589	1.5
4A	40	23.1	0.418	1.54
4A	60	57.8	0.387	1.51
4A	80	141	0.397	1.51
5A	20	10.4	0.594	1.47
5A	40	25.9	0.468	1.51
5A	60	66.9	0.448	1.48
5A	80	186	0.524	1.46

Figure 1 graphs the Barney [1] results, as well as the solubility of aluminate in solution observed in the pure NaOH-NaAl(OH)$_4$-H$_2$O system. Figure 1 is commonly denoted as the "Barney Diagram" at the Hanford site. The gibbsite solubility data in simple NaOH solutions shown in Figure 1 is from reference [17] whereas the sodium aluminate solubility data is from reference [8]. There are several significant aspects of this plot. The most striking observation is that the dissolved aluminum concentration was much higher in the simulated Hanford saltcake supernatants than in the pure NaOH-NaAl(OH)$_4$-H$_2$O in the composition region where the solubility is controlled by gibbsite. The rest of this paper will seek to explain this enhanced solubility. Sodium aluminate is less soluble in tank waste than in pure NaOH solutions because of the common ion effect.
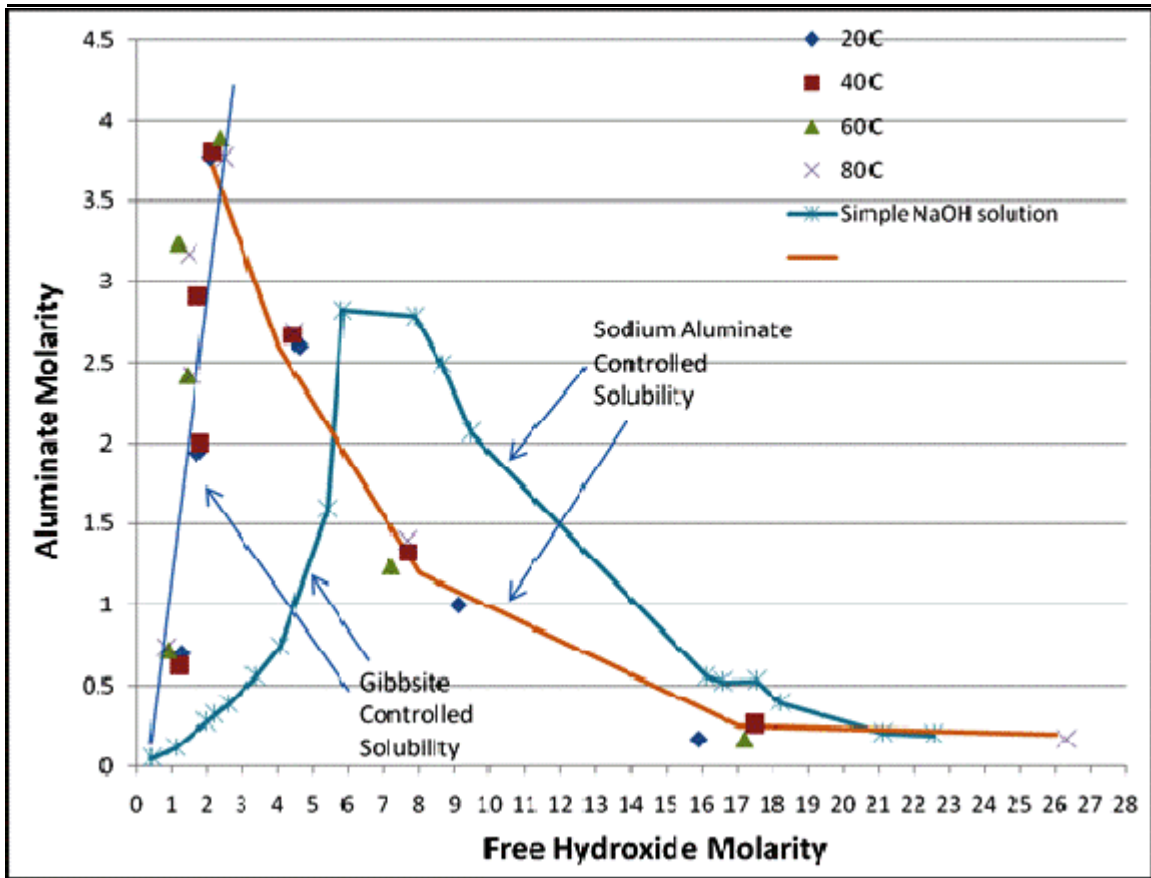
Fig.1. The Barney Diagram of Aluminum Solubility.

INTERPRETATION OF THE BARNEY DATA

Sodium Aluminate Ion-Pairs

Here we hypothesize that sodium-aluminate ion pairs are likely present in the Barney data, constituting a second species of aluminum in solution in addition to the aluminate ion. The presence of an additional species will effectively increase the solubility of aluminum because aluminum can partition into several species. The sodium aluminate ion-pair would be created in solution by the following reaction:

$$Na^+_{(aq)} + Al(OH)^+_{4\,(aq)} \leftrightarrow NaAl(OH)_{4\,(aq)} \tag{Eq. 6}$$

Note that the sodium aluminate product in Equation 6 is a dissolved species rather than the solid in Equation 4. The free ions in the left hand side of Equation 6 are each hydrated with water molecules, the sodium hydrated between 4 and 6 water molecules [18], the aluminate ion being more weakly hydrated [19]. An ion-pair is essentially just the free ions bound together without water molecules in-between in the liquid phase. Marcus [20] has shown that some highly concentrated salt solutions do not have enough space for a water molecule in-between the ions, and thus there must be at least some ion-

pairs in those solutions. Marcus [20] derived Equation 7 as a method to calculate the average distance between the centers of the ions in solution:

$$d = 0.940\left(\frac{1}{M}\right)^{(1/3)} \hspace{4cm} \text{(Eq. 7)}$$

In Equation 7, d is the average distance between the center of the anion and cation in nanometers, M is the molarity of the solution. The average diameter of a water molecule is 0.276 nm, so there must be at least 0.276 nm for a water molecule in between the ions in order to avoid ion-paring in solution. The sodium molarities reported by Barney are between 10.6 and 19. Substituting these molarities into Equation 7 results in a range of 0.35 and 0.43 nm between the centers of the cations and anions in the Barney simulants. These distances, however, are the distance between the center of the ions, so the radius of the cation and anion must be subtracted from these distances in order to determine if there is sufficient space for a water molecule (on average). Sodium, the lone cation, has an ionic radius of 0.123 nm [21]. The molar weighted average anion radius was calculated from the mole fractions of each anion in the simulant and the radii of each anion [19, 21]. This average anion radius came to be between 0.137 nm and 0.168 nm with the difference depending on the relative quantity of each anion in Table I. Adding the sodium radius to the anion radius and subtracting the result from the average distance between the ions calculated above shows that there is between 0.052 and 0.163 nm of space between the cation and anion in these solutions. Consequently, there is insufficient room for a 0.276 nm water molecule in between the cations and anions in the Barney simulants. Therefore, at least half of the cations and anions in the solution must form an ion-pair.

Even though there is insufficient space for a water molecule between ions "on average" within the tank waste simulants studied by Barney (1976), there must be water between some of the ions. If there were no water between any ions, there would be no water in the solution. We cannot be certain that aluminate is forming an ion-pair with sodium from this analysis. We can be certain, however, that most of the ions in solution in the Barney simulants are ion-paired, so it would be reasonable to expect that at least some of the aluminum in solution exists as an ion-pair. Indeed, sodium aluminate ion-pairs have been identified in simple sodium hydroxide solutions [19]. The authors cannot verify that there is more sodium aluminate ion pairing in the Barney simulants than in simple sodium hydroxide solutions. Nonetheless, this is a reasonable assumption, given the much higher sodium concentration in the Barney simulants at a given free hydroxide concentration.

Dimer Formation

The aluminate dimer [$(OH)_3Al-O-Al(OH)_3{}^{2-}$] has been known to exist in high pH solutions for a long time but is a minor species in pure sodium hydroxide solutions [9]. The reaction to form this dimer from the aqueous aluminate ion is:

$$2Al(OH)_4^- \leftrightarrow (OH)_3 Al - O - Al(OH)_3^{2-} + H_2O \qquad \text{(Eq. 8)}$$
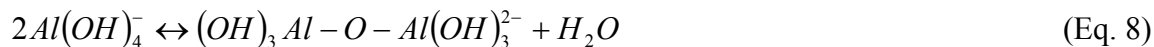
As can be seen from this reaction, the aluminate dimer is increasingly favored as the water activity is decreased because water is created on the right side of the equation. The creation of the dimer is a dehydration reaction that would be favored in solutions with little water because the reaction creates water. The Barney simulants had low water contents. In the region of enhanced gibbsite solubility (< 3 molar free hydroxide), the water content of the Barney simulants were between 36.2 and 45.4 weight percent. In contrast, a 3 molar solution of pure NaOH is greater than 90 weight percent water. Therefore, the dimer would be expected to be more prevalent in Barney's simulants than in simple sodium hydroxide solutions at the same free hydroxide concentration.

Thermodynamically, the impact of the water content of the waste on the equilibrium is expressed through the water activity. The water activity in a solution is the vapor pressure of the solution divided by the vapor pressure of pure water at the same temperature [11]. The water activities were calculated here from the vapor pressures reported by Barney [1] and are shown in Table II. For the region of the Barney diagram with enhanced gibbsite solubilities, the water activity was calculated to be between 0.38 and 0.5, with most near 0.42 (water activity is in units of vapor pressure over vapor pressure of pure water). The total aluminum molalities of those same samples were between 3 and 7 molal. Figure 4 of Sipos [9] conveniently fractioned the dissolved aluminum between aluminate and the dimer at a water activity of 0.4. According to that figure in Sipos [9], at 0.4 water activity and total aluminum molalities between 3 and 7, the fraction of dimeric aluminum in solution is between 30 and 50 mol-%. In contrast, the fraction of the dimer in simple sodium hydroxide solutions at the same free hydroxide concentration is less than 5% [9]. Thus, it can be concluded that the aluminum dimer likely accounts for a substantial fraction of the total aluminum in the simulants prepared by Barney and is a significant contributor to the high relative solubility observed by Barney [1]. Hence, some of the aluminum is partitioned into this dimer species in addition to the aluminate ion. This conclusion is consistent with the modeling approach of Reynolds [22], who assumed that gibbsite solubility would increase substantially as the water activity decreases because of changes in speciation.

Kinetics

Barney [1] equilibrated his samples for three to seven days, attempting to approach equilibrium from only the super-saturation direction. Herting and Clevenger [23] demonstrated that four weeks was required to achieve equilibrium in simulated waste supernatant samples at 80 ºC from supersaturation, and the rate decreased as the ionic strength increased. The ionic strength effect observed by Herting and Clevenger [23] is consistent with the work of others [24], who studied gibbsite precipitation kinetics in simple hydroxide solutions. The ionic strength of the Barney simulants was considerably higher than those studied by Teslya et al. [24] or Herting and Clevenger [23], suggesting that equilibrium would take more than four weeks to achieve at 80 ºC for the Barney simulants. Additionally, much of the Barney data is below 80 ºC, so the kinetics would be expected to be even slower. Therefore, it is unlikely that the studies of Barney

reached equilibrium in just seven days, and the data probably does not reflect true equilibrium conditions in the gibbsite portion of the curve. This is in contrast to the sodium aluminate portion of the curve, where equilibrium is achieved in just 2 days [25].

DISCUSSION

To summarize the conclusions of this paper, the enhanced solubility of gibbsite observed by Barney [1] is likely attributed to three different sources. One source is the likely enhanced formation of sodium aluminate ion-pairs in solution. The second source is the formation of the aluminate dimer. The third source is likely slow gibbsite precipitation kinetics. However, the real answer is probably more complicated than this. For instance, can the dimer form ion-pairs? How does the presence of the dimer and the sodium aluminate ion-pair influence precipitation kinetics? Do these species enhance or inhibit gibbsite precipitation kinetics? Hence, what do the dimer and the ion-pair do to the assumption that the aluminum did not achieve equilibrium? Is it really fair to compare the kinetics in these solutions to Herting and Clevenger [23], or simple NaOH solutions such as those studied by Teslya [24] that may have smaller concentrations of the dimer and the ion-pair? In addition to just precipitation kinetics, how do these other species influence dissolution kinetics? Dissolution kinetics is important for understanding how waste dissolves during waste treatment processes. Furthermore, if the Barney simulants did not reach equilibrium with the solid phase, can we really assume the liquid phase speciation has reached equilibrium? If the liquid speciation has not reached equilibrium, can we still conclude that the dimer and the sodium aluminate ion pair are significant species in the Barney simulants at equilibrium? For instance, would the dimer still be significant if there was less aluminum in solution? These questions remain unanswered, but are crucial to the application of the Barney data to new situations. For instance, if there is a kinetics limitation to the precipitation rate of gibbsite, one would certainly not want to depend on gibbsite remaining supersaturated longer than the seven day equilibration period used by Barney [1] in any flowsheet.

Correct thermodynamic evaluation of gibbsite solubility depends on the exact quantity of the sodium-aluminate ion-pair and the aluminate dimer in solution. These quantities could not be quantitatively determined in the present study. Nonetheless, our ability to quantify these species governs our ability to extrapolate Barney's results to other waste compositions. Consequently, there are still questions about the interpretation of the Barney [1] study that cannot be answered by the current data. If the Barney data is repeated, the experimenters should include approaching equilibrium from both under-saturation and supersaturation so that we can be sure that all solutions reach equilibrium. Likewise the aluminate dimer should be quantified in solution, which can be performed through the Raman spectroscopic method of Johnston et al. [10]. Quantifying sodium-aluminate ion-pairing is more difficult. However, the extent of this ion-pairing may be quantifiable based on the deviation of the solubility experiments from predictions that do not include the ion-pair, after accounting for the presence of the aluminate dimer.

CONCLUSIONS

The enhanced apparent solubility of gibbsite observed by Barney [1] is likely attributed to three different sources. One source is the likely enhanced formation of sodium aluminate ion-pairs in solution. The second source is the formation of the aluminate dimer. The third source is likely slow precipitation kinetics, as compared to the data of Herting and Clevenger [23]. If the Barney experiments were to be repeated, the authors recommend approaching equilibrium from both under and over-saturation while measuring the concentration of the dimer.

ACKNOWLEDGMENTS

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