Aluminum Solubility Model for Hanford Tank Waste Treatment - 9123

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ABSTRACT

The solubility of aluminum in Hanford tank waste is a critical issue that fundamentally impacts the planning basis for treating waste at Hanford's Waste Treatment Plant. Dissolving or leaching aluminum from Hanford tank sludges and maintaining its solubility during pretreatment requires the addition of large amounts of sodium hydroxide. Recent estimates suggest that added sodium may result in nearly doubling the amount of Low-Activity Waste (LAW) [1]. On the other hand, aluminum (as aluminate) often shows very high solubility in Hanford tank waste supernatants. There are many reports of tank farm supernatants with aluminum concentrations in the range of 0.2 to 1.5 M, considerably higher than predicted by current models with the measured free hydroxide concentrations. This paper proposes an aluminum solubility model that is consistent with these observations by taking into account not only the free hydroxide, but three additional characteristics of these complex waste mixtures: 1) Low water activity that appears to stabilize aluminate in solution and is caused by high amounts of dissolved salts in waste concentrates; 2) Carbonate appears to further stabilize aluminate in solution; and 3) High TOC (total organic carbon) in waste also appears to stabilize soluble aluminate. This paper shows this "water activity" aluminum solubility model is consistent with a large number of tank farm assays and may therefore be useful for Site planning.

INTRODUCTION

The solubility of aluminum (Al) in aqueous sodium hydroxide has been developed and studied for well over a century. The reason for this is its key importance for Al extraction from bauxitic ores [7]. For caustic defense nuclear wastes at Hanford and Savannah River Sites Al solubility is an important factor for effective reduction of immobilized high level waste (IHLW). In the past at Hanford Site during the production of defense radioisotopes, two processes resulted in most tank waste Al. First, caustic dissolution of nuclear fuel cladding (Al metal) and second, the caustic neutralization of raffinates containing the $Al(NO_3)_3$ salting agent for the first solvent extract process at Hanford, Redox.

Dissolving Al cladding involved oxidation with a caustic nitrate solution that resulted in the soluble aluminate, termed cladding waste (CW). The decladding process added 3,495 MT of Al (41% of total) to an ever growing number of large waste tanks over the course of Hanford's operating history. The Redox acid raffinate, comprising both fission products as well as Al, chromium, and other species, was neutralized with NaOH and sent to a set of boiling waste tanks where it cooled for several years. After 2-3 years of cooling, these wastes were further manipulated by extraction of Cs and Sr and evaporative concentration into "saltcake" solids. The result today is an additional 4,090 MT Al (48% of total), which

along with some other Al sources results in a total of 8,525 MT Al in Hanford Site waste tanks today. This aluminum is present in both soluble and insoluble forms, some forms of which are well understood and some not so well understood.

During future processing at Hanford's Waste Treatment and Immobilization Plant (WTP), dissolution of insoluble waste aluminum will be very important in order to minimize the production of immobilized high level waste glass. Furthermore, adequate prediction of aluminum solubility as a function of hydroxide and other species present will be very important in planning that will minimize both immobilized low activity waste (ILAW) and other secondary wastes.

Aluminum solubility in the simple system of three components, NaOH, $Al(OH)_3$, and H_2O, has a reported solubility curve shown in Fig. 1 as a red line [2]. This simple model forms the basis for Al solubility for many applications, and in particular, for the Hanford WTP. Figure 1 also shows Al concentrations for 60 reported supernatants among the 177 Hanford waste tanks [8], comprising a dataset that shows Al concentrations that are many times those of the Apps curve.

For the BBI data in this plot, the free hydroxide is calculated by charge balance from the equation

$$[OH\text{-}]_{ffree} = [Na] - [Al] + 3*[Bi] + 2*[Ca] + 3*[Cr] + 3*[Fe] + 2[Hg] + [K] + 3[La] + 2[Mn] + 2[Ni] + 2[Pb] - [Si] + 2*[Sr] - 0.4[TOC] + 4*[Zr] - [Cl] - 2*[CO3] - [F] - [NO2] - [NO3] - 3*[PO4] - 2*[SO4] + 6*[U] \qquad [A]$$

resulting in a free hydroxide range of 0.0 to 5.5 M for the 60 tanks. There are six tanks where this is negative (ranging from -0.18 to -1.2M) and we assumed [OH⁻] = 0.0 and increased sodium to balance. This calculation was necessary since the hydroxide is not reported within the BBI dataset but also because it is necessary to have an ion-balanced and mass balanced dataset for this analysis.
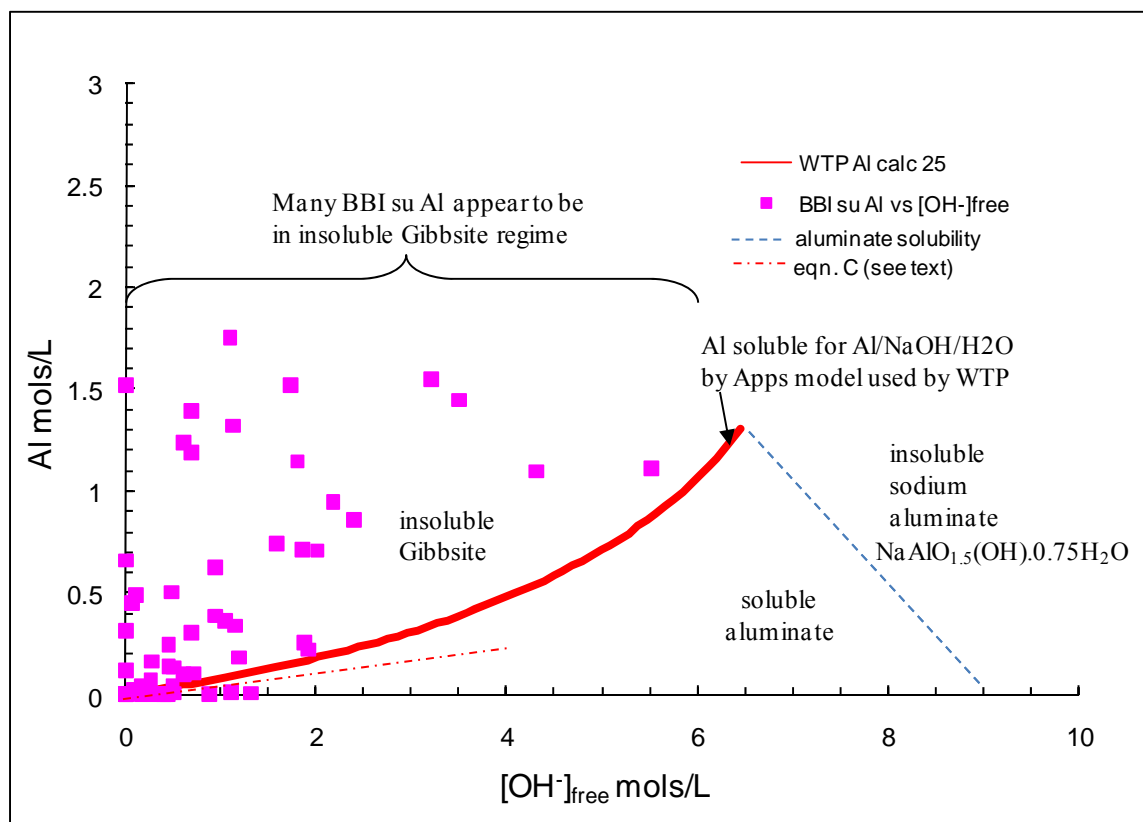
Fig. 1. Plot showing Apps [2] solubility at 25 C (solid red line) versus free hydroxide. Also shown are BBI supernatant Al concentrations (purple boxes), equilibrium Al solubility from eqn. C (dot-dash red line), and boundary for insoluble aluminate (dashed blue line).

As is evident from Fig. 1, the solubility of Al above the simple Apps curve seems to be the norm for Hanford tanks supernatants. It is clear that using the Apps curve to predict Al solubility in Hanford tank waste will likely overestimate the WTP sodium demand by a large amount. It is therefore desirable to have an Al solubility model that is more appropriate to Hanford waste complexity.

METHODOLOGY

In its simplest form, gibbsite or Al(OH)3 solubility is

$$Al(OH)_3(solid) + OH^- <> Al(OH)_4^- \qquad [B]$$
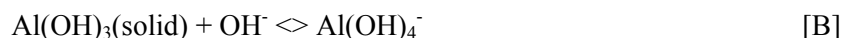
and this expression shows up in much previous work [2,10]. The corresponding equilibrium constant is from Table I

$$K_{eq} = [Al(OH)_4^-] / [OH^-] = 0.059 \qquad [C]$$

show a linear relationship between free hydroxide and soluble Al (dot-dash red line in Fig. 1). This simple expression explains neither the curvature of the Apps solubility nor that of the tank waste data. Therefore, all reports show substantially greater Al solubility at increasing hydroxide concentrations as compared to eqn. [C].

Table I.   Thermodynamic Constants.

species	ΔG^o_f	ΔH^o_f	Keq
Gibbsite, $Al(OH)_3$	-1154.8	-1289.1	
$Al(OH)_4^-$	-1305.0	-1496.2	
OH-	-157.2	-230.0	
net	-7.0	-22.9	0.059
h_a Russell fit		-32.0	
h_b Russell fit		2.0	
$Al(OH)_3 \cdot H_2O$		-1298.2	

We propose a very simple model that shows that the decreasing water activity associated with increasing hydroxide is consistent with increasing Al solubility shown in Fig. 1. Reynolds [9] showed that gibbsite solubility in tank waste is highly dependent on the water activity. Furthermore, reported [4] water activity impacts both speciation and activity coefficients for dissolved species. Gibbsite is a sparingly soluble molecular solid, so ionic strength does not directly affect its stability. Rather, gibbsite solubility is linked to hydroxide and water activities, here modeled as

$$Al(OH)_3 \cdot H_2O + OH^- <> Al(OH)_4^- + H_2O. \qquad [D]$$
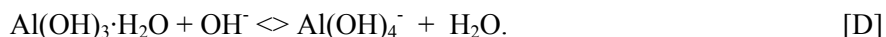
Ionic strength *per se* does not appear in [D] directly. Rather changes in water activity, which are certainly related to ionic strength among other factors, affect aluminate solubility. For example, increasing water activity *increases* the [D] back reaction and *decreases* solubility. The expression $\{Al(OH)_3 \cdot H_2O\}$ models the solvated form of aluminum hydroxide (i.e. gibbsite), not a solid hydrate, and its activity is assumed = 1, i.e., constant concentration independent of water or aluminate. This equilibrium expression is then

$$k_1 = K_{eq} = [Al(OH)_4^-] \{H_2O\}_{act} / [OH^-] \qquad [E]$$

which upon using water activity as

$$\{H_2O\}_{act} = 1 - k_2(1 - mol\%H_2O) \qquad [F]$$

where the water mol% of the solution is

$$mol\%H_2O = 1 / (1 + ([Na] + [Al] + [CO_3] + [OH])*18.015/wt\%H_2O/\rho, \qquad [G]$$

given ρ, the solution density, in g/L. Note that this implies the reaction

$$H_2O_{free} <> H_2O_{bound}. \qquad [H]$$
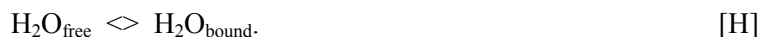
Solving for aluminate [E] becomes

$$[Al(OH)_4^-]= [OH^-]_{total} * 1/(1 + 1/k_1 - k_2/k_1*(1-mol\%H_2O)) \qquad [I]$$

which for free or excess hydroxide the expression becomes

$$[Al(OH)_4^-]= [OH^-]_{free} * 1/(1/k_1 - k_2/k_1*(1-mol\%H_2O)). \qquad [J]$$

This very simple expression is consistent with measured data as shown in Figure 1 (solid red line with k_1 = 0.059, k_2 = 2.2) reported for HTWOS model [6, Fig. 4-1]. The values for k_1 and k_2 are fit to this dataset and show that in addition to hydroxide (k_1 factor), reduction of water activity (k_2 factor) seems to play a major role in enhancing aluminate solubility.

For ideal solutions, the water activity (fugacity or percent relative humidity, %RH) of a solution is equal to the water mol fraction, or $k_2 \sim 1.0$. For any real solution, though, water activity is reduced from that ideal by a variety of inner and outer sphere complexation with other species, hydrogen bonding effects, and other solvation dynamics.

Figure 2 shows reported relative humidity (%RH) [5] as a function of mol%H_2O for solutions containing NaOH, NaAl(OH)$_4$, Na$_2$CO$_3$, and water. Here the water activity or %RH decreases much more rapidly than for an ideal solution, and the fit of that data is

$$\{H_2O\}_{act} = 1 \ - \ (k_2(1- mol\%H_2O))^{k3} \qquad\qquad [K]$$
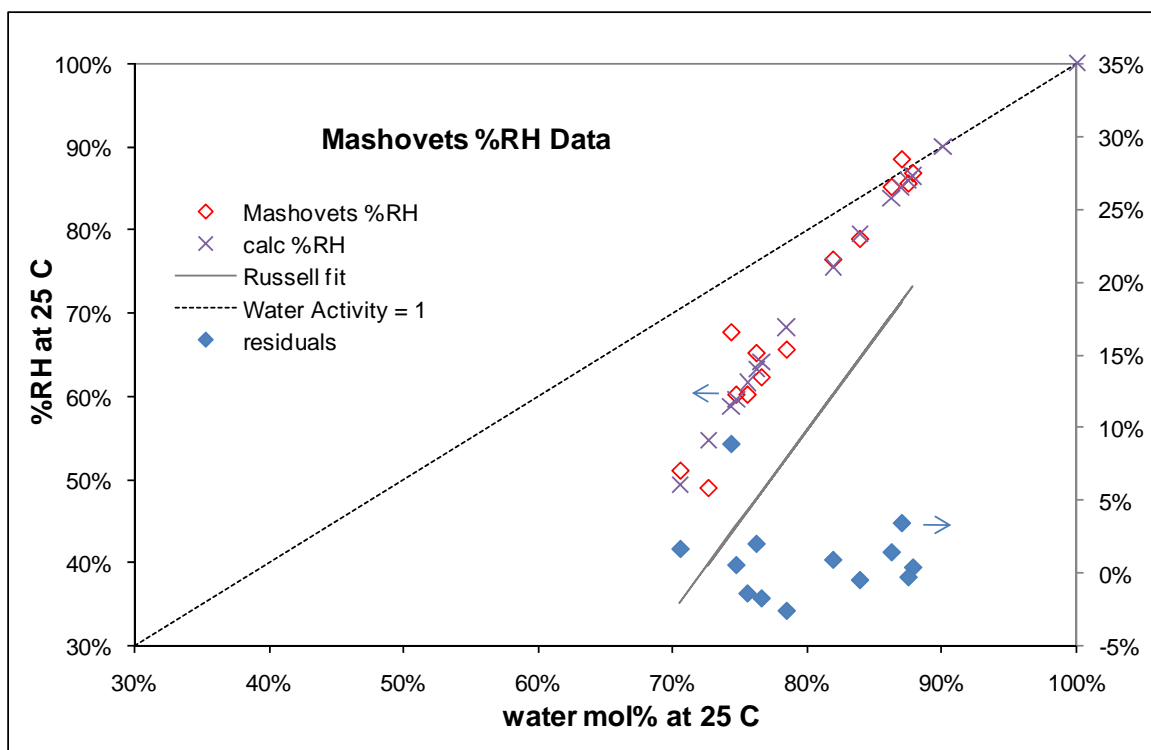
where k_2 = 2.15 and k_3 = 1.5.

Fig. 2. Plot of %RH vs. water mol% from Mashovets and calculations (X) as shown.

To fit gibbsite solubility data from Russell, et al. [11] for all its temperature ranges, we need two additional parameters:

h_a = enthalpy for reaction [D], competition between hydroxide and water for gibbsite complexation.

h_b = enthalpy for reaction [H], reduction of water activity.

Incorporating these enthalpies into [I, J] results in

$[Al(OH)_4^-] = [OH^-]_{total} * 1/(1 + e^{ha(1/298-1/T)/R}/k_1 - e^{(ha-hb)(1/298-1/T)/R}k_2/k_1*(1-mol\%H_2O))$ [L]

$[Al(OH)_4^-] = [OH^-]_{free} * 1/(e^{ha(1/298-1/T)/R}/k_1 - e^{(ha-hb)(1/298-1/T)/R}k_2/k_1*(1-mol\%\%H_2O))$ [M]

RESULTS AND DISCUSSION

For total and free hydroxide, respectively. Figure 3 shows the result of fitting Russell's data with the set of parameters

$k_1 = 0.059$
$k_2 = 2.8$
$h_a = -32.0$ kJ/mol
$h_b = 2.0$ kJ/mol .

The expression for water activity used eqn. [F], which Fig. 2 shows as a solid line. It appears that the water activity needed for fitting [L] is more strongly dependent on mol%H$_2$O than the %RH data from similar solutions.
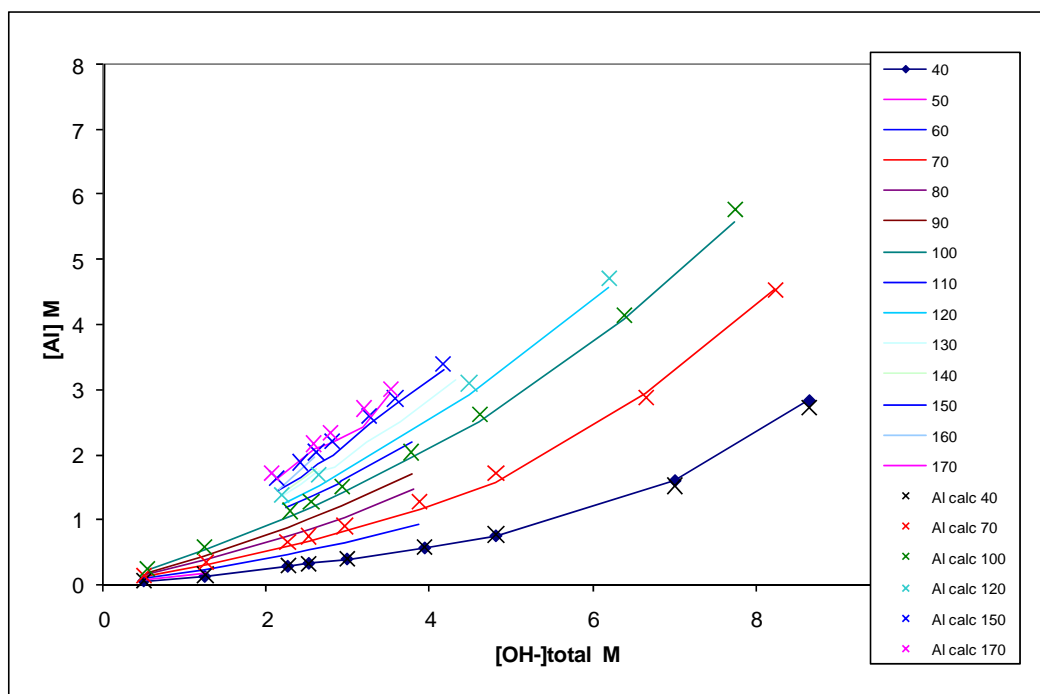

Fig. 3. Al solubility versus total hydroxide at temperatures (ºC) shown by Russell, et al. [11] data (solid diamonds and lines) and calculated (X) with eqn. [L] and parameters shown in text.

The fit is quite good over the entire temperature range for such a simple model. The enthalpy (h_a) for reaction [D] is exothermic, suppressing the rate with increasing temperature while h_b for reaction [H] is mildly endothermic.

We find that much of the Al solubility of waste can be explained with this water activity expression even for quite complex waste compositions. This water-activity model provides a basis for adjusting Al solubility by reduction in water activity due to many different species such as nitrate and nitrite, not just hydroxide and aluminate [13]. However, there appear to be other factors as well as hydroxide and water activity for explaining enhanced Al solubility. In particular, tank waste contains large amounts of NaNO$_3$

and $NaNO_2$ as well as Na_2CO_3 (as TIC) and organic carbon as TOC.   In fact, the TOC comprises numerous soluble chelates in the waste that can complex aluminum [12].

The role of soluble carbonatoaluminates in enhancing Al solubility, for example, can not be ruled out. Carbonatoaluminates are quite well known as solids and appear to be very stable in solution under the right conditions [5]. Mashovets measured aluminate solutions saturated with carbonate with aluminum concentrations much higher than those observed in simpler systems [2].

Such an effect of carbonate is twofold in that it increases ionic strength, thereby reducing water activity and it complexes aluminum in solution. Since the carbonatoaluminate complex may in principle release two equivalents of hydroxide as

$$Al(OH)_4^- \ + \ CO_3^{2-} \ -> \ Al(OH)_2CO_3^- \ + \ 2OH^- \qquad\qquad [N]$$
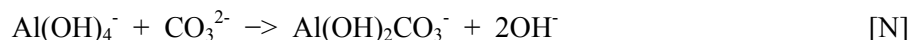
which effectively multiplies its impact since the resultant free hydroxide will solubilize even more Al. To extend the simple expression for aluminate solubility [J] we add two terms as

$$[OH\text{-}]_{free} + 4[TIC] + 3[TOC] \qquad\qquad [O]$$

giving

$$[Al] = ([OH\text{-}]_{free} + 4[TIC] + 3[TOC])/(1/k_1 - k_2/k_1*(1\text{-}mol\%H_2O)). \qquad\qquad [P]$$

This expression can be used to model the concentrations of aluminum reported by the Best Basis Inventory [8]. Using this expression along with the values

$k_1 \ = \ 0.059$
$k_2 \ = \ 2.4$

we find a reasonable set of Al solubility predictions for the BBI supernatants. Figure 4 shows the residuals or differences between that calculation and the reported Al solubility as a function of the term [O], which includes hydroxide as well as carbonate as TIC and organic carbon as TOC.

Figure 5 shows BBI supernatant data plotted versus the hydroxide/TIC/TOC expression [O] with a locus of Al solubility sketched in with dashed lines. This locus represents an enhanced Al solubility incorporating the effects of not only hydroxide, but also water activity, TIC, and TOC.

Also shown are data from earlier work [3] (open circles) versus hydroxide alone showing very high Al solubility for waste surrogates. These surrogates incorporated nitrate, nitrite, and carbonate all at or near saturation. Once Barney's data is plotted versus the extended hydroxide/TIC/TOC expression [O] (solid circles), it coincides with the locus Al solubility for tank waste supernatants.
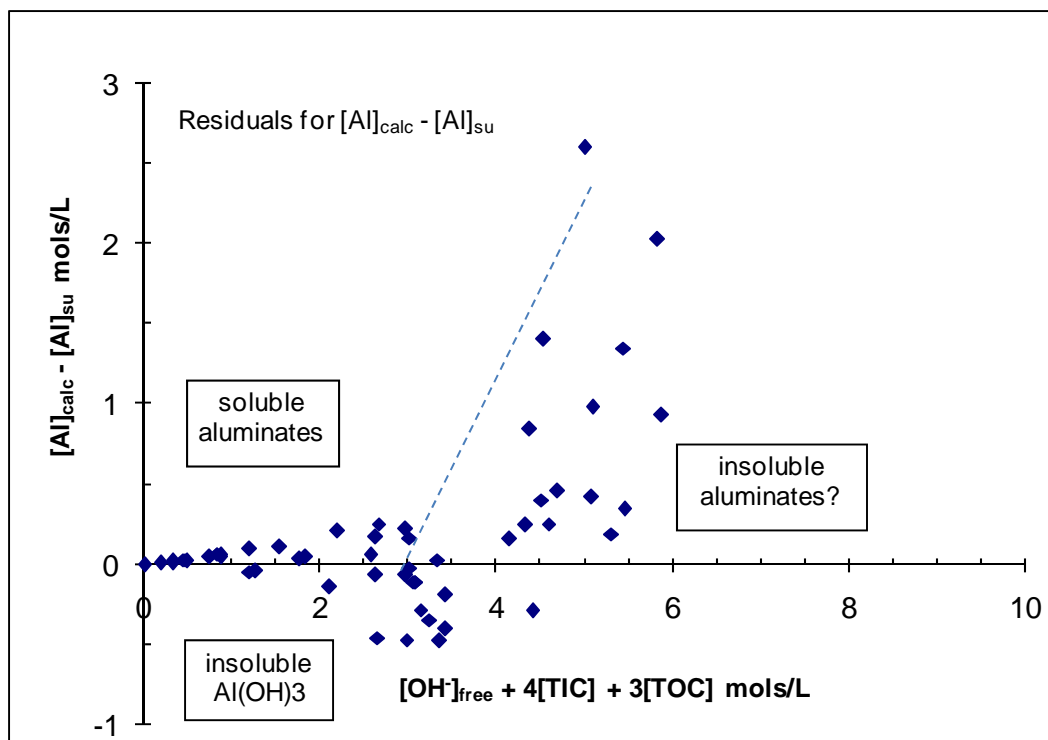
Fig. 4. Plot of residuals for Al calculated solubility minus the BBI reported Al for each of 60 tank supernatants. This plot is a function of the hydroxide/TIC/TOC expression.
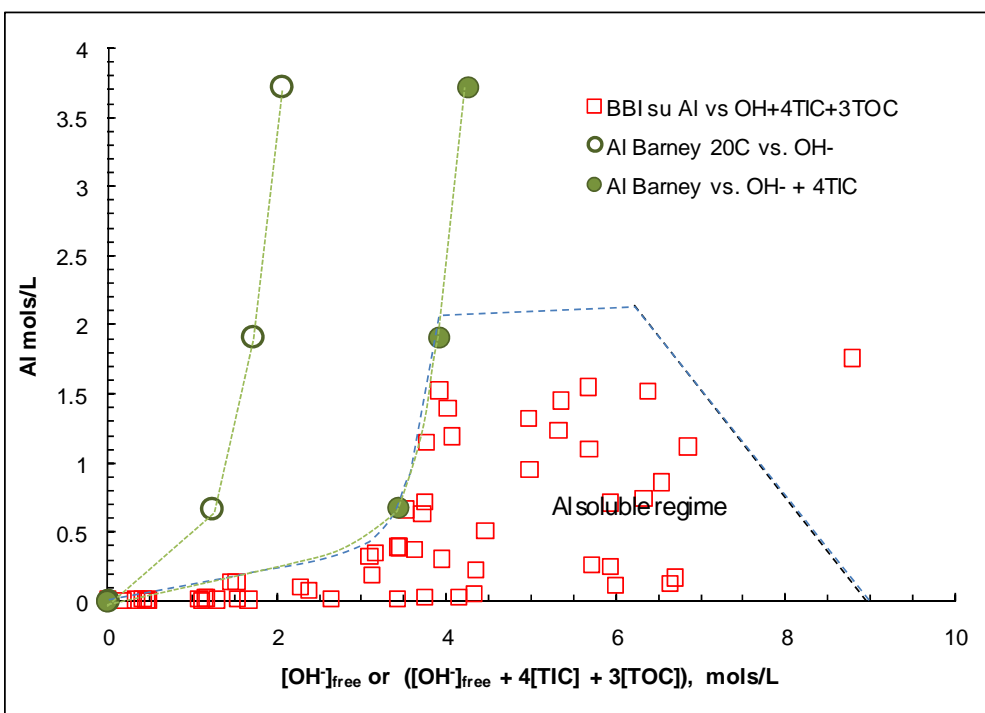

Fig. 5. Plot showing a locus of Al solubility (squares) for 60 complex tank waste supernatants. Also data from earlier work [3] (open circles) plotted versus hydroxide alone shifts into this locus when plotted versus hydroxide/TIC/TOC.

SUMMARY

The well-known dependence of Al solubility on hydroxide concentration occurs by means of formation of soluble aluminate, $Al(OH)_4^-$. Although it has also been long recognized that changes in species activities are important for highly concentrated sodium hydroxide solutions, the role of water activity has not yet been well defined. The water-activity model herein developed seems to be consistent with the large amount of data for the simple system of NaOH, $Al(OH)_3$, and H_2O, including temperature. Moreover, this paper shows additional roles for carbonate (TIC) and TOC for enhancing Al solubility in Hanford waste concentrates. If validated, the water-activity model could prove very useful in waste treatment planning not only at Hanford, but at Savannah River Site as well.

ACKNOWLEDGEMENTS

REFERENCES

1. 24590-WTP-MRR-PET-08-002rev1, July 2008, *WTP Contract Run*, Bechtel Hanford (BNI).
2. Apps, J. A., J. M. Neil, and C.-H. Jun. 1989. *Thermochemical Properties of Gibbsite, Bayerite, Boehmite, Diaspore, and the Aluminate Ion Between 0 and 350˚C*, NUREG/CR--5271, Lawrence Berkeley Laboratory, Berkeley, CA.
3. Barney, G. S., *Vapor-Liquid-Solid Phase Equilibria of Radioactive Sodium Salt Wastes at Hanford,* ARH-ST-133, Atlantic Richfield Hanford Company, Richland, WA, 1976.
4. Johnston, C. T.; Agnew, S. F.; Schoonover, J. R.; Kenney, III, J. W.; Page, B.; Osborn, J.; Corbin, R., *Raman Study of Aluminum Speciation in Simulated Alkaline Nuclear Waste,* Environ. Sci. Technol., 36 (11), 2451-8, 2002.
5. Mashovets, V.P.; Penkina, N.V.; Puchkov, L.V.; Kurochkina, V.V., *Vapor Pressure and Densities of Caustic Soda and Sodium Aluminate Solutions with Additions of Sodium Carbonate at 25-300ºC*, Z. Prikladnoi Khimii, 44, 7, pp. 1550-3, 1971, English Translation.
6. Meacham, J.E., *Aluminum Wash and Leach Factors*, RPP-11079, Rev. 0, 2003.
7. Misra, C., *Industrial Alumina Chemicals,* ACS Monograph 184, American Chemical Society, Washington, DC, 1986.
8. PNNL-SA-45730, *TWINS database,* July 2007. This is where the BBI came from.
9. Reynolds, D. A., *Practical Modeling of Aluminum Species in High-pH Waste*, WHC-EP-0872, Westinghouse Hanford Company, Richland, Washington, 1995.
10. RPP-06-003, Rev.1, *Baseline Change Request Alignment of TFC Lifecycle Baseline*, CH2M HILL Hanford Group, Inc., Richland, Washington, 2006.
11. Russell, A.S.; Edwards, J.D.; Taylor, C.S., *Solubility and Density of Hydrated Aluminas in NaOH Solutions,* J. Metals, 1123, Trans. American Inst. Metallurgical Eng., 1955.
12. Toste, A.P.; Osborn, B.C.; Polach, K.J.;Lechner-Fish, T.J. *Organic Analyses of an Actual and Simulated Mixed Waste: Hanford's Organic Complexant Waste Revisited*, J. Radioanal. Nucl. Chem., 194, 1, 1995.
13. Zemaitis, J. F., Clark, D. M., Rafal, M., Scrivner C. N., *Handbook of Aqueous Electrolyte Thermodynamics*, AICHE: New York, NY, 1986.