

Role of Dawsonite in Aluminum Solubility for Hanford Tank Waste Treatment- 10323

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ABSTRACT

Dissolving or leaching aluminum (Al) from Hanford tank sludges and maintaining Al solubility during pretreatment requires the addition of sodium hydroxide. There are a range of estimates for the amount of sodium hydroxide needed, but the fact remains that aluminum (as aluminate) often shows very high solubility in Hanford tank waste supernatants even before adding additional hydroxide. The Hanford TWINS (Tank Waste Information Network) database, for example, reports ~1500 assays of tank liquids with Al greater than 1000 ppm and ranging as large as 3.4 M. It now appears that in many tank waste liquids the solid dawsonite, $\text{NaAl}(\text{OH})_2\text{CO}_3$, is more stable than gibbsite and this is responsible for the increased Al solubility in Hanford tank liquids.

Much of the past work on Al solubility has focused on the role of gibbsite, bayerite, or boehmite solids on limiting Al solubility. Indeed, tank sludge assays show that insoluble Al is largely gibbsite and boehmite with dawsonite as a minor fraction. Nevertheless, tank liquid assays are consistent with the thermodynamic solubility limit for dawsonite, not gibbsite. This paper discusses the resulting indirect role of carbonate in Al solubility, i.e. carbonate does not change the form of Al in solution but rather carbonate alters the form of precipitated Al.

INTRODUCTION

Previous reports [1,2] showed that despite the many predictions based on gibbsite solubility, aluminum is much more soluble in Hanford tank waste liquids as compared with simple gibbsite hydroxide solutions. Hanford's Best-Basis Inventory (BBI), which is based on appropriately weighted tank assays as well as other waste process estimates, reports Al solubility in tank farm supernatants, for example, that are much greater than the gibbsite model predictions. As a result, there was a large uncertainty in Al solubility [3] and therefore a significant uncertainty in sodium hydroxide demand for WTP to stabilize Al in solution.

Because of the key importance of Al extraction from bauxitic ores [4,5], the solubility of Al in aqueous sodium hydroxide has been studied for well over a century. It is therefore surprising that there appears to be so much uncertainty in Al solubility for caustic defense nuclear wastes at Hanford and Savannah River Sites. For these Sites, Al solubility is an important factor for effective reduction of immobilized high level waste (IHLW).

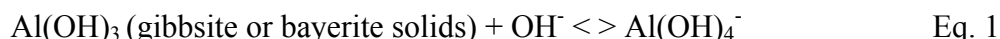
The enhanced Al solubility in Hanford waste liquids has been often attributed to the high ionic strength of these solutions. Indeed, tank waste concentrates can often exceed 10 M Na and show Al solubility greater than 2 M Al. However, repeated investigations of high ionic strength effects do not appear to show substantial effects due to ionic strength [6,7]. On the other hand, other work has shown that suitably complex simulants do show enhanced Al solubility although the specific factors were not further delineated [8].

A more recent study [3] presents further details for Al solubility based on the Hanford TWINS assay dataset [9]. This analysis shows Al solubility is more complicated and it appears that Al solubility in Hanford wastes is related to dawsonite, $\text{NaAl}(\text{OH})_2\text{CO}_3$, instead of gibbsite or bayerite, $\text{Al}(\text{OH})_3$. Dawsonitic Al introduces a greater compositional dependence for Al solubility since dawsonite solubility depends not only on hydroxide (second order instead of gibbsite first order) but also *inversely* on sodium and carbonate. This dawsonitic Al solubility limit is much more consistent with reported tank waste liquid assays than the gibbsitic limit.

For more concentrated solutions, there are other important factors for Al solubility including the role of water activity and the presence of the aluminate dimer [3], but these factors will not be discussed in this paper.

METHODOLOGY

In its simplest form, gibbsite or bayerite ($\text{Al}(\text{OH})_3$) solubility is



and this expression shows up in much previous work [1,5]. Given a desired Al concentration, the corresponding expression for the free hydroxide concentration demand is

$$[\text{OH}^-] = [\text{Al}(\text{OH})_4^-] / K_{\text{eq}} \quad \text{Eq. 2}$$

Where K_{eq} can be a range between 0.076 and 0.16 depending on whether gibbsite or the bayerite solids form [5,6,7]. This shows a linear relationship between free hydroxide and soluble Al (dot-dash red line in Fig. 1). All concentrations are represented with either brackets as $[\text{X}]$ or as subscripted C_x for species X and units are molarity, M (mols/L). Solids are all assumed to have unit activities and other activity corrections are ignored.

However, the “effective” free hydroxide demand even in this simple system shows a marked non-linearity and in particular,

$$[\text{OH}^-] = C_{\text{Al}} / 0.081 - b C_{\text{Al}}^2 / 0.13 + b^2 C_{\text{Al}}^3 / 0.66 \quad \text{Eq. 3}$$

is used [10,11] by the Hanford Waste Treatment and Processing Plant (WTP) to determine the sodium hydroxide demand for stabilizing Al liquids at 25 C and 5 M total Na. The standard conversion to molal from molar is $b = 1/(\rho - \sum(C_x \cdot m_{w_x})/1000)$, where ρ is density in g/cm^3 , C_x is molar concentration of species X, and m_{w_x} is the molecular weight of species X. This dependence is based on the well-known solubility limits for gibbsite or bayerite in the simple three component mixtures of NaOH, $\text{Al}(\text{OH})_3$, and H_2O , with some adjustment for ionic strength effects of Hanford waste at 5 M Na.

Figure 1 shows the Al versus measured hydroxide concentrations for 683 tank liquid assays from the TWINS dataset along with hydroxide calculated by Eq. 2 and Eq. 3. For a large number of liquid assays, Al solubility exceeds the gibbsite limit for Eq. 3 and there are a number of assays reported above 2.0 M Al, which is an order of magnitude greater than gibbsite Al solubility predictions. Figure 1 also shows a solubility calculation for Dawsonite (circles) which is described below.

Dawsonite, $\text{NaAl}(\text{OH})_2\text{CO}_3$, is a sodium carbanatoaluminate salt that has been observed in Hanford wastes although gibbsite is more often reported [12]. Dawsonite is a fairly rare natural mineral [13] that is nevertheless stable under certain conditions, which are reportedly very high

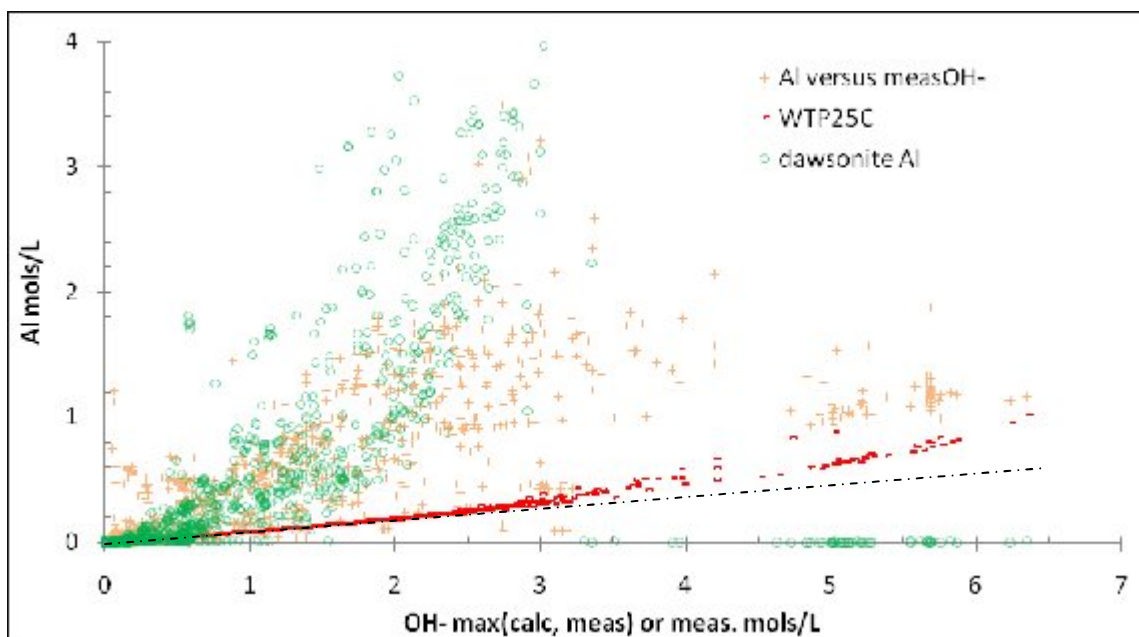
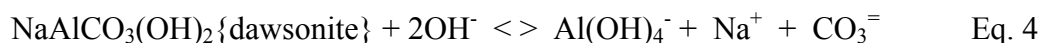


Fig. 1. Plot showing measured Al assays versus hydroxide (crosses) along with the calculation for dawsonite (circles), WTP gibbsite Al solubility limits (solid red line), and linear relation (dot-dash line) cited in text.

CO_2 partial pressures [14]. Dawsonite has also been made simply by adding sodium carbonate to a slurry of amorphous $\text{Al}(\text{OH})_3$ [15] and it appears in tank wastes with high carbonate concentrations along with aluminate, sodium, and free hydroxide.

Soluble Al in the presence of dawsonite is more complex [16] than gibbsite as



where the “dawsonitic” hydroxide demand is now

$$[\text{OH}^-] = \sqrt{C_{\text{Al}} C_{\text{Na}} C_{\text{CO}_3}} / K_3 / (C_{\text{Al}} + C_{\text{Na}} + C_{\text{OH}} + C_{\text{CO}_3}), K_3 = 0.14, 25 \text{ C} \quad \text{Eq. 5}$$

which is calculated recursively since $C_{\text{OH}} = [\text{OH}^-]$. Alternatively, the closed form expression is slightly more complex as

$$[\text{OH}^-] = \sqrt{[(C_{\text{Al}} + C_{\text{Na}} + C_{\text{CO}_3})^2 + 4\sqrt{C_{\text{Al}} C_{\text{Na}} C_{\text{CO}_3}} / K_3] - (C_{\text{Al}} + C_{\text{Na}} + C_{\text{CO}_3})} / 2 \quad \text{Eq. 6}$$

In addition to the dawsonitic NaOH demand, there is also a dawsonitic sodium carbonate demand as

$$C_{\text{CO}_3} = \text{Max}[C_{\text{CO}_3\text{min}}, K_3 C_{\text{OH}}^2 / C_{\text{Na}} / C_{\text{Almax}} (C_{\text{Na}} + C_{\text{Almax}} + C_{\text{OH}} + C_{\text{CO}_3})] \quad \text{Eq. 7}$$

with $C_{\text{CO}_3\text{min}} = 0.2 \text{ M}$ and $C_{\text{Almax}} = 0.8 \text{ M}$.

Sufficient carbonate keeps the solution in the dawsonitic Al regime, which is where carbonate concentration is greater than $C_{\text{CO}_3\text{min}}$ and soluble Al is less than C_{Almax} for Na in the range 3 to

6 M. The rationale for this carbonate demand and aluminate limit is thus far empirical and will be discussed later.

Finally, the Dawsonitic Al solubility limit is simply

$$[\text{Al}(\text{OH})_4^-] = K_3 C_{\text{OH}}^2 (C_{\text{Al}} + C_{\text{Na}} + C_{\text{OH}} + C_{\text{CO}_3}) / (C_{\text{Na}} C_{\text{CO}_3}), K_3 = 0.14, 25 \text{ C} \quad \text{Eq. 8}$$

which ranges from second to third order in hydroxide and is inversely dependent on both sodium and carbonate and plotted in Fig. 1.

RESULTS AND DISCUSSION

It seems apparent that the dawsonitic limit for Hanford tank waste Al solubility is much more representative of waste liquids than the gibbsitic limit as shown in Fig. 1. Figure 2 shows a more limited set of TWINS Al assays versus free hydroxide only for those assays with the sodium range $3 < [\text{Na}] < 6 \text{ M}$. Also shown are gibbsitic Eq. 3 and dawsonitic Eq. 8 Al solubility limits given for TWINS measured hydroxide, sodium, and carbonate assays.

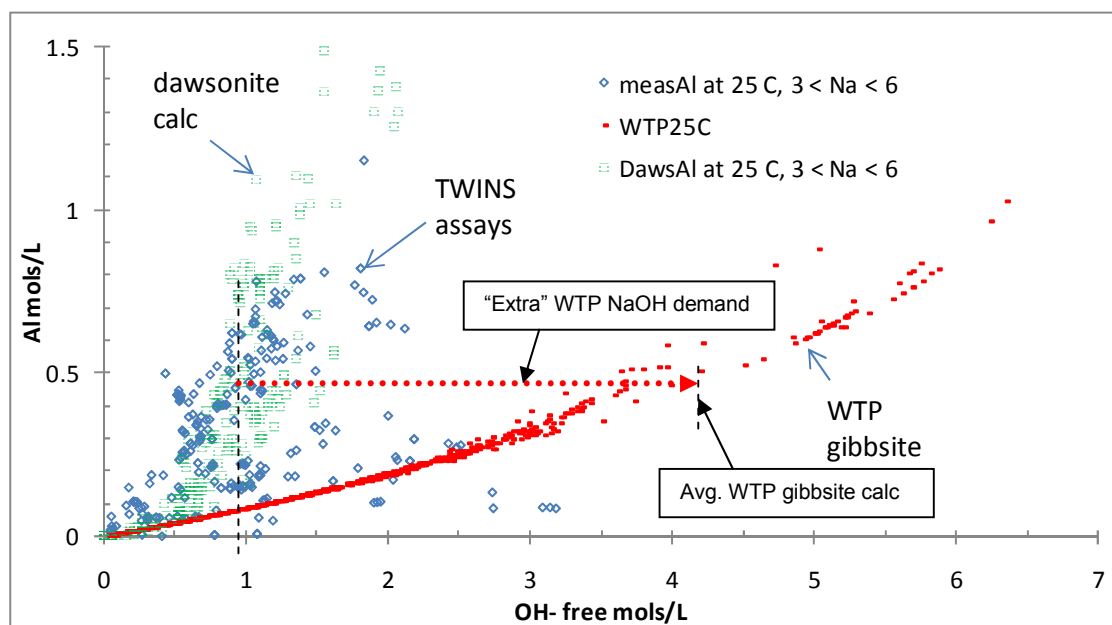


Fig. 2. Plot showing TWINS data (diamonds) for Na between 3 and 6 M. Also shown are dawsonitic (squares) and WTP (red line) calculations. The dawsonitic calculation seems to agree better with many measured tank waste assays. Since tank liquids may not be saturated, overprediction of solubility is still consistent with the model.

These calculations have not included any activity effects, i.e., corrections for the non-ideal nature of concentrated solutions. Nevertheless the correlation of Al solubility in waste liquids with that calculated for solutions in equilibrium with dawsonite is quite remarkable. Moreover, it would appear that the WTP Al solubility calculation based on gibbsitic solutions may be as much as a factor of four greater NaOH demand. The dotted red arrow in Fig. 2 shows the difference in measured hydroxide and measured Al at 0.5 M Al for Hanford waste liquids and the gibbsite calculation. This analysis appears in more detail elsewhere [3].

Indeed previous measurements [8] of Al solubility in complex waste surrogates showed very high Al solubility for prepared solutions that were similar to waste tank concentrates. These very high Al solubilities have never been completely explained but have nevertheless been used for various tank waste studies.

Figure 3 shows that Al “Barney” [8] data is more consistent with dawsonitic Al solubility data than with gibbsitic Al. Once again, even though there are no activity corrections in these dawsonitic calculations the agreement is quite good.

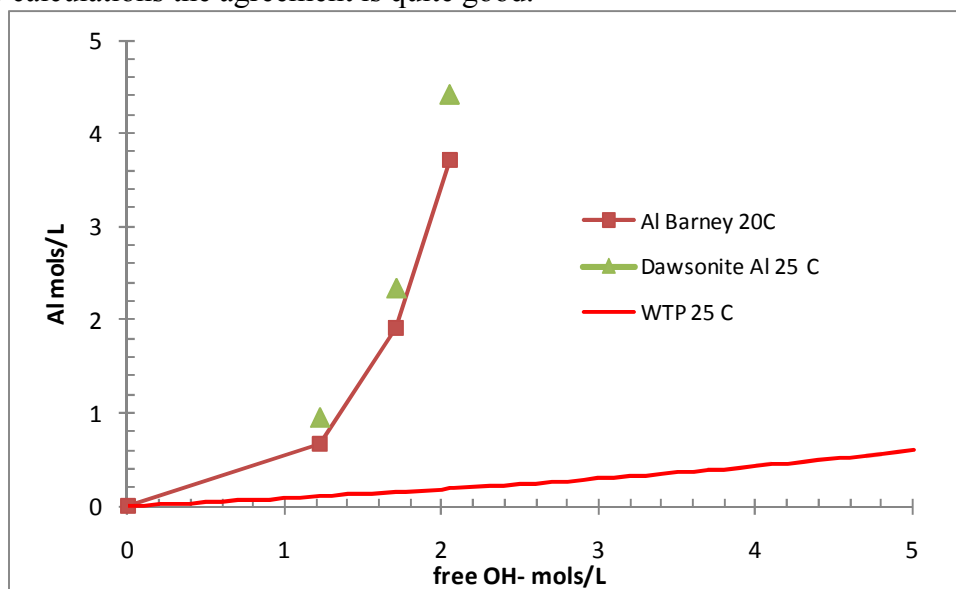


Fig. 3. Plot comparing the dawsonitic and gibbsitic calculations with previous data [8].

Interestingly, as either sodium or carbonate concentrations decrease, Eq. 8 for dawsonitic Al solubility grows arbitrarily large. What this means is that there regimes of stability for dawsonite and gibbsite and Fig.4 shows TWINS assays of carbonate versus aluminate for the same TWINS dataset in Fig. 1. It appears that there is a definite locus of Al solutions associated with the dawsonitic solubility as indicated in Fig. 4.

Presumably above the carbonate threshold there is sufficient solution carbonate to sustain a dawsonitic Al solubility. Limiting aluminate below its threshold likewise prevents aluminate from competing with the surface carbonate on active dawsonite crystals, thereby sustaining dawsonitic Al solubility within this range of carbonate and aluminate.

Correspondingly, for carbonate below the threshold or aluminate above its threshold, the gibbsite solubility limit once again dominates. There is also a sodium range in which these data have been validated, 3 to 6 M Na. These explanations are reasonable and consistent with the information presented, but remain otherwise unproven.

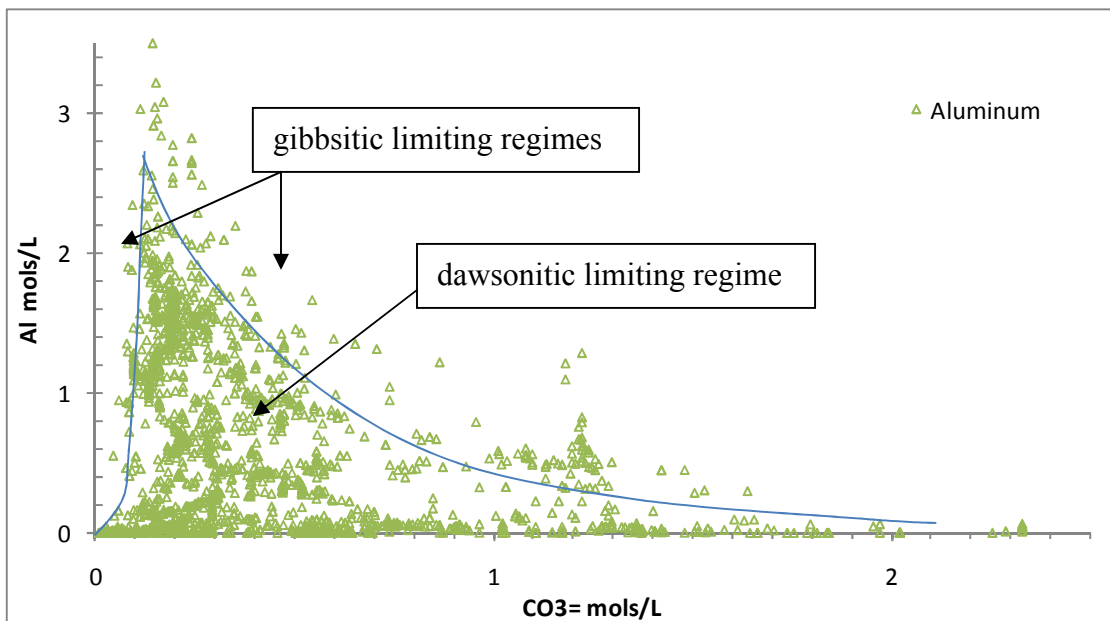


Fig. 4. Plot shows measured Al concentrations versus carbonate. This locus of carbonate and aluminate within the lines defines the dawsonitic versus gibbsitic limiting solubility regimes for waste liquids.

Figure 5 shows the stability regime for the simple three component system, dissolved Al, free hydroxide, and water, from various sources [17,18,19] along with OLI ESP/MSE fits (solid lines) given adjusted activity functions[20]. The ESP fits appear to be valid only below ~ 2.0 M Al.

Also shown is a mapping of the dawsonitic stability regime for Hanford waste liquids, which includes dependencies on both sodium and carbonate, which range as noted above.

Having Al in coexisting solids, gibbsite, bayerite, and dawsonite, with such different solubility properties presents a level of complexity that it is beyond most homogeneous solubility models. It is therefore perhaps understandable that this problem has remained obscured until now. In other words, the fact that these solid crystals coexist also implies a host of intermediate solids, in effect one solid phase encapsulating or coating another phase. The nature of these mixtures would depend on the particular history of that waste's concentration.

Despite the quite complex interdependencies that have been used in previous aluminate activity functions, it is surprising that this simple dawsonitic model explains so much so well. Nevertheless, there is still plenty of room for improvement that would now include activity for not only aluminate, but the aluminate dimer as well.

The dawsonitic carbonate and aluminate limits derived here are empirically determined from the TWINS assay dataset. Thus far, there is no physical basis for either of these limits, but it is likely that they are related to the properties and chemistry of gibbsite and dawsonite crystal surfaces, both existing and nucleating.

Presumably above the carbonate threshold there is sufficient solution carbonate to “passivate” all surface “aluminate” on growing and nucleating gibbsite crystals, thereby sustaining a dawsonitic Al solubility. Limiting aluminate below its threshold likewise prevents aluminate from competing with the surface carbonate on active dawsonite crystals, thereby sustaining dawsonitic Al solubility.

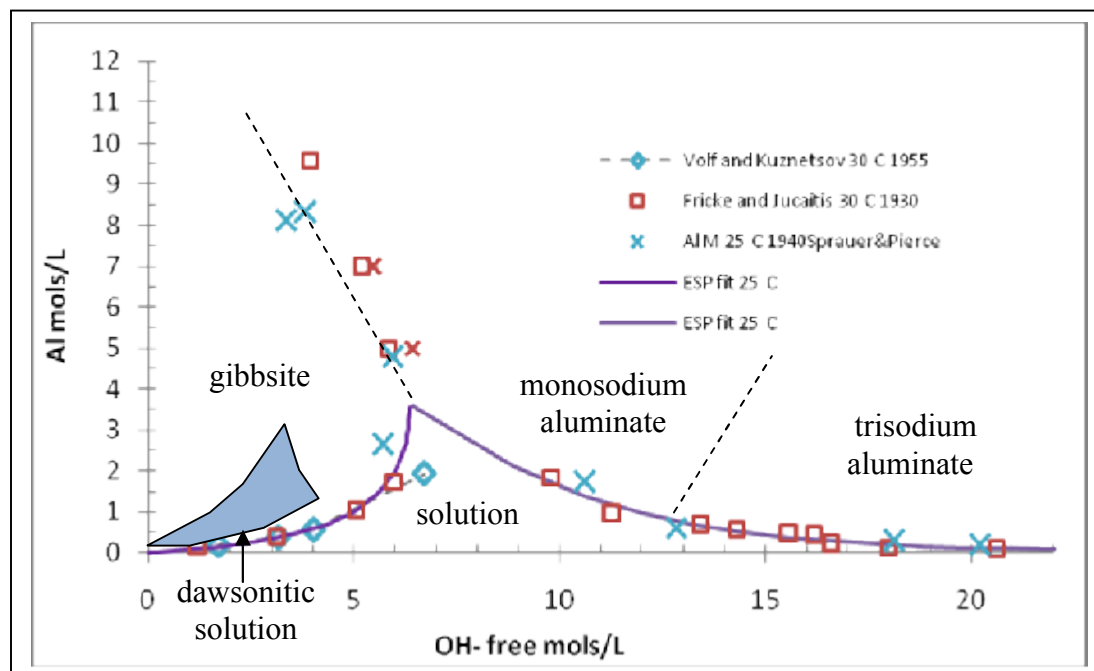


Fig. 5. Plot of Al solubility from various sources as well as the OLI ESP/MSE regression lines. Dashed lines sketch in gibbsite and monosodium aluminate. Also shown is “mapping” of the dawsonitic regime for Hanford waste soluble Al that includes additional sodium and carbonate.

Correspondingly, for carbonate below the threshold or aluminate above its threshold, the gibbsite solubility limit dominates. There is also the sodium range in which these data have been validated, 3 to 6 M Na. It is quite likely that sodium also plays a role in the surface chemistry. These explanations are reasonable and consistent with the information presented, but remain otherwise unproven.

Finally, one might ask a very simple question. Since gibbsite is much less soluble than either dawsonite or even bayerite at 25 C, why does gibbsite not precipitate and therefore control Al solubility in any event? A simple answer is related to the thermodynamic stability of each solid relative to the species present in solution. Given carbonate and sodium in contact with solids, dawsonite is simply more thermodynamically stable than gibbsite. In addition, there is the complexity of the interfaces between the solids and solutions and interfaces among the solids, both for nucleating as well as growing crystallites. These combined thermodynamic and kinetic effects can be quite complex even in simple mixtures. Given the complexity of tank waste liquids, these effects can become quite difficult to model.

SUMMARY

The well-known dependence of Al solubility on hydroxide concentration occurs by means of formation of soluble aluminate, $\text{Al}(\text{OH})_4^-$. Although it has also been long recognized that changes in various species activities are important for more complex highly concentrated sodium hydroxide solutions, the role of these other species activities has not always been well defined. In particular, the potential role of carbonate in stabilizing dawsonitic Al and enhancing Al solubility proposed herein, certainly should be further validated. Although solids were not identified, continuously variable aluminate concentrations far in excess of gibbsite were reported in a study that explored the solidification of Hanford simulants by addition of CO_2 [21].

The approach described here for dawsonitic Al solubility depends on thermodynamic constants that are published in the literature and includes no corrections for activity. The only parameters used were those for defining the carbonate stability range, which were trained to the TWINS assay dataset.

The Hanford tank waste liquid assays definitely correlate with dawsonitic Al, but since waste compositions are complex, it could be that there is another species in the waste and that species also correlates with carbonate. The sources of waste carbonate are largely from atmospheric CO_2 capture and from oxidation of TOC and therefore carbonate is highly correlated with other species associated with these waste types.

ACKNOWLEDGEMENTS

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