

# The Apparent Solubility of Aluminum(III) in Hanford High-Level Waste

Prepared for the U.S. Department of Energy  
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy  
Office of River Protection under Contract DE-AC27-08RV14800



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12 **ABSTRACT**  
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14 The solubility of aluminum in Hanford nuclear waste impacts on the processability of the waste  
15 by a number of proposed treatment options. For many years, Hanford staff has anecdotally noted  
16 that aluminum appears to be considerably more soluble in Hanford waste than the simpler  
17 electrolyte solutions used as analogues. There has been minimal scientific study to confirm these  
18 anecdotal observations, however. The present study determines the apparent solubility product  
19 for gibbsite in 50 tank samples. The ratio of hydroxide to aluminum in the liquid phase for the  
20 samples is calculated and plotted as a function of total sodium molarity. Total sodium molarity is  
21 used as a surrogate for ionic strength, because the relative ratios of mono, di and trivalent anions  
22 are not available for all of the samples. These results were compared to the simple  
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NaOH-NaAl(OH)<sub>4</sub>-H<sub>2</sub>O system, and the NaOH-NaAl(OH)<sub>4</sub>-NaCl-H<sub>2</sub>O system data retrieved from the literature. The results show that gibbsite is apparently more soluble in the samples than in the simple systems whenever the sodium molarity is greater than two. This apparent enhanced solubility cannot be explained solely by differences in ionic strength. The change in solubility with ionic strength in simple systems is small compared to the difference between aluminum solubility in Hanford waste and the simple systems. The reason for the apparent enhanced solubility is unknown, but could include kinetic or thermodynamic factors that are not present in the simple electrolyte systems. Any kinetic explanation would have to explain why the samples are always supersaturated whenever the sodium molarity is above two. Real waste characterization data should not be used to validate thermodynamic solubility models until it can be confirmed that the apparent enhanced gibbsite solubility is a thermodynamic effect and not a kinetic effect.

**Keywords:** Hanford, nuclear waste, aluminum solubility, gibbsite.

## INTRODUCTION

Aluminum(III) is one of the most prevalent constituents in high-level nuclear waste stored in 177 tanks at the Hanford site in Richland, Washington. Given the large quantities of Al(III) in the waste, the solubility of Al(III) affects the performance of most waste treatment options. Indeed, several recent independent review groups noted that improved Al(III) solubility models were required to optimize tank waste cleanup activities.<sup>[1-4]</sup> The most direct impact of Al(III) solubility on waste separation processes is through caustic leaching of gibbsite [Al(OH)<sub>3</sub>] from

waste sludge.<sup>[5]</sup> Additionally, Al(III) precipitation can foul ion-exchange columns, evaporators, and filters. Any model of Al(III) solubility will eventually have to be validated against real waste behavior. A similar approach has been undertaken to validate Al(III) solubility models for the Bayer process,<sup>[6]</sup> which is a high-pH, high-ionic strength system like Hanford waste. An obvious way to start developing an improved model is to look at the apparent solubility of Al(III) exhibited by the waste itself. That is the purpose of the present study.

The dominant aluminum species in the aqueous phase of caustic Hanford high-level waste is believed to be the aluminate anion  $[\text{Al}(\text{OH})_4^-]$ , although the aluminate dimer is also present.<sup>[7, 8]</sup> Gibbsite and boehmite are assumed to be the most prevalent aluminum-bearing solids in Hanford tank waste.<sup>[9]</sup> Dawsonite  $[\text{NaAl}(\text{OH})_2\text{CO}_3]$  and aluminosilicates have recently been identified in a few tanks as well.<sup>[10, 11]</sup> Boehmite has extremely slow dissolution and precipitation kinetics at current tank temperatures,<sup>[12, 13]</sup> so boehmite is assumed to have a negligible impact on the liquid phase aluminum concentration. Therefore, gibbsite precipitation has historically been assumed to limit the liquid phase aluminum concentration of Hanford nuclear waste.

In addition to Al(III), Hanford waste has large quantities of sodium, nitrite, nitrate, carbonate, hydroxide, sulfate, phosphate, iron, manganese, uranium, zirconium, bismuth, many organics, and many other less prevalent constituents.<sup>[14]</sup> These components may affect the solubility of Al(III) in the tank waste. For instance, the soluble species would be expected to affect the ionic strength, which, in turn, has a major impact on the solubility of practically every other species.<sup>[15]</sup> Sodium, being the dominant cation in the liquid phase, typically has a concentration between one and 12 molar.

74

75 Given the large concentration of dissolved hydroxide in waste, the solubility of gibbsite in  
76 Hanford waste has traditionally been compared to gibbsite solubility in simple aqueous solution  
77 of sodium hydroxide. There is a large amount of gibbsite solubility data available in these simple  
78 sodium hydroxide solutions.<sup>[16]</sup> In 1976, Barney<sup>[17]</sup> discovered that the apparent solubility of  
79 gibbsite was as much as ten times higher in simulated Hanford waste supernatant solutions than  
80 in simple  $\text{NaOH}_{(\text{aq})}$  of the same hydroxide concentration. The reason for this difference has been  
81 hotly debated ever since.<sup>[18]</sup> Barney only studied simulants with sodium concentrations greater  
82 than 10 M Na, and did not study any real waste samples. Reynolds<sup>[19]</sup> determined that the  
83 solubility of gibbsite in Barney's study could not be modeled accurately without invoking new  
84 liquid phase aluminum species. Like Barney,<sup>[17]</sup> Reynolds<sup>[19]</sup> addressed waste simulants rather  
85 than real waste samples. Therefore, the apparent solubility of real waste needs to be evaluated, to  
86 determine if real waste also exhibits this apparent enhanced solubility. Since the time of Barney,  
87 Hanford laboratory staff has periodically noted dissolved aluminum concentrations that  
88 "seemed" elevated for real waste, but there has been minimal in-depth study of the enhanced  
89 solubility.

90

91 A more recent modeling study by Agnew<sup>[20]</sup> proposed that  $\text{Al(III)}$  concentrations in tank  
92 samples were more consistent with the solubility of dawsonite than gibbsite. Dawsonite is more  
93 soluble than gibbsite. Thus, Agnew<sup>[20]</sup> noted that the apparent solubility of real tank waste is  
94 considerably higher than simple  $\text{NaOH}_{(\text{aq})}$  solutions in equilibrium with gibbsite. These results  
95 are consistent with the simulant work performed by Barney<sup>[17, 18]</sup> more than 30 years ago. There  
96 were some limitations with Agnew's<sup>[20]</sup> work, however. For instance, he often determined the

dissolved hydroxide concentration in waste samples by charge balance. A recent study has determined that charge balance calculations on Hanford waste are frequently biased, and require a special methodology for reconciliation.<sup>[21]</sup> Charge balance calculations are also affected by species with unknown charge, such as “total organic carbon” measurements. Agnew<sup>[20]</sup> converted analytical data from mass per volume units to molality units using water contents calculated by the method of Reynolds and Carter.<sup>[22]</sup> That method depends heavily on the accuracy of the concentration of the constituents, including the hydroxide concentrations. Thus, errors in the hydroxide concentrations measured by charge balance are magnified molality units through the density conversion equation. The limitations with Agnew’s<sup>[20]</sup> study has left many in the scientific community skeptical of his results.<sup>[2-3]</sup> The purpose of the present study is to verify Agnew’s<sup>[20]</sup> conclusion that Al(III) is much more soluble in Hanford tank waste than in simple NaOH<sub>(aq)</sub> solutions of similar hydroxide concentration in equilibrium with gibbsite. This study will determine the apparent solubility product for gibbsite in tank waste as indicated by waste sample data. The term “apparent” is used because confirmation of equilibrium with gibbsite is not determinable from the present data (see discussion section).

## METHODOLOGY

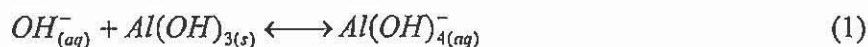
Taking a statistically designed approach of sampling Hanford tanks is infeasible because of the high cost of taking samples of highly radioactive tank waste. Thus, this study uses existing sample data. The Hanford waste tanks have been sampled and analyzed for many different reasons and these data are used here opportunistically. The Hanford site maintains the Tank Waste Information Network System (TWINS) database that keeps all of the analytical data on



120 tank waste generated since year 1992. For this study, TWINS database was queried to find all  
121 samples where the sodium, aluminum, and hydroxide concentrations were measured on the same  
122 liquid samples. Exactly fifty data points in TWINS met these criteria, and these results are shown  
123 in Table 1. Aluminum was measured by Inductively Coupled Plasma Atomic Emission  
124 Spectroscopy in all cases, and was assumed to be in the form of the aluminate ion.

126 Most analytical data on nuclear waste liquids are reported by the laboratory in units of mass per  
127 volume (here converted to moles per liter). Ideally, a comparison of different Al(III) solubility  
128 datasets would be performed in units of molality (moles per Kg of water), because molality is  
129 independent of the concentration of other electrolytes in the mixture.<sup>[15,23]</sup> Densities and water  
130 contents are required for the conversion from molarity to molality, however, and are not  
131 available for most of the data evaluated here. Consequently, volume units (moles/L) are used  
132 here to maximize the amount of data in the comparison. In order to overcome the limitation of  
133 using molarity units, hydroxide to Al(III) ratios were compared rather than concentrations.  
134 Ratios are independent of concentration scale,<sup>[23]</sup> so comparisons of ratios are not degraded by  
135 using molarity units.

137 The apparent solubility product for aluminum will be expressed relative to the mineral gibbsite  
138  $[\text{Al}(\text{OH})_3]$ , because gibbsite is the most prevalent solid identified in Hanford waste.<sup>[9]</sup> The term  
139 “apparent” is used because confirmation of equilibrium with gibbsite is not determinable from  
140 the present data (see discussion section). The reaction between gibbsite and dissolved hydroxide  
141 to create aluminate is written as Equation 1.



From this reaction stoichiometry, the dissolved hydroxide to aluminate ratio defines the inverse of the apparent equilibrium constant (here denoted as 1/Q to distinguish it from a true equilibrium constant that is usually denoted K). This ratio also defines the number of hydroxide moles required to keep one mole of Al(III) soluble, a quantity of interest to engineers trying to prevent the precipitation of Al(III) during filtration and ion-exchange. The lower the 1/Q for a sample, the higher the apparent solubility of gibbsite exhibited. Table 1 provides this ratio for sample data taken from TWINS. The concentrations in Table 1 represent the means of duplicate analyses on each sample, or the ratio of the means. These results are compared to the solubility of gibbsite in simple NaOH<sub>(aq)</sub> and NaCl<sub>(aq)</sub>- NaOH<sub>(aq)</sub> liquids, as described below.

The OH:Al ratio at equilibrium with gibbsite is influenced by solution ionic strength.<sup>[16,24]</sup> The ionic strength range of Hanford waste varies widely. In order to account for ionic strength, 1/Q is plotted against the sodium molarity in Figure 1 of the tank waste samples, with sodium molarity being used as a surrogate for ionic strength. The data from Li et al.<sup>[25]</sup> at 25 °C are also plotted on Figure 1, as a dataset that has only NaOH<sub>(aq)</sub> and no other electrolytes. The NaOH-NaAl(OH)<sub>4</sub>-NaCl-H<sub>2</sub>O system data presented by Wesolowski<sup>[16]</sup> represents a slightly more complicated system, with an additional electrolyte influencing ionic strength besides NaOH and NaAl(OH)<sub>4</sub>. Wesolowski<sup>[16]</sup> presented his data in molality units, so his sodium concentrations are not directly comparable to the molarity units used on the X-axis in Figure 1. Thus, his data was converted to molarity units using densities calculated by the method of Reynolds and Carter.<sup>[22,26]</sup>

## RESULTS AND DISCUSSION

One/Q (one over the apparent solubility product for gibbsite) is plotted in Figure 1 as a function of sodium molarity for multi-electrolyte Hanford tank waste, along with the simple NaOH-NaAl(OH)<sub>4</sub>-H<sub>2</sub>O<sup>[25]</sup> and NaOH-NaAl(OH)<sub>4</sub>-NaCl-H<sub>2</sub>O systems.<sup>[16]</sup> The value for 1/Q is the number of moles of hydroxide that are in solution per mole of Al(III) dissolved. When these solutions are at equilibrium at standard state,  $1/Q = 1/K$ , where  $K$  = the equilibrium constant for the reaction in Equation 1. Figure 1 indicates that the apparent gibbsite solubility is much higher in the overwhelming majority of the tank waste sample in this study than in the simpler NaOH-NaAl(OH)<sub>4</sub>-H<sub>2</sub>O and NaOH-NaAl(OH)<sub>4</sub>-NaCl-H<sub>2</sub>O systems in equilibrium with gibbsite. This is evidenced by the fact that most of the hydroxide to Al(III) ratios for Hanford waste are lower than those given by the simple systems at a given sodium molarity. The only exceptions are at sodium molarities below two. These results are consistent with Agnew's<sup>[20]</sup> conclusion that gibbsite appears more soluble in tank waste than in simple systems. This conclusion is also consistent with the original simulant data reported by Barney<sup>[17, 18]</sup> more than 30 years ago. Barney<sup>[17]</sup> only studied highly concentrated solutions (10.5 to 19 M). From the current results, however, we can discern that Barney's<sup>[17]</sup> conclusions extend down to the lower concentrations.

Several aspects of Figure 1 must be discussed in detail. The simple system data plotted in Figure 1 were collected at 25 °C.<sup>[16, 25]</sup> Temperature monitoring data in the Hanford's TWINS database indicate that the tank temperatures ranged from 18 to 45 °C, with all but three data points below 35 °C. Wesolowski<sup>[16]</sup> collected data at both 25 and 50 °C, which bound the upper

end of the tank temperature range, though most of the tank samples are closer to 25 °C than 50 °C. The hot cell that the samples are stored in prior to analyses (for sometimes up to several months) is roughly 28 °C. Some of the Hanford data points do lay above the 50 °C Wesolowski <sup>[16]</sup> data on Figure 1, indicating that high tank temperature could potentially account for high solubility in some samples. Nonetheless, the majority of the data lays below the 50 °C Wesolowski <sup>[16]</sup> data in Figure 1, indicating that temperature is unlikely to explain the majority of the difference between the tank waste data and the simple system data.

In Figure 1, sodium molarity was used on the X-axis as an indicator of ionic strength. In the simple system data, <sup>[16, 25]</sup> all of the ions were monovalent, so the ionic strength would be identical at a given sodium molarity (assuming no ion-pairing). Real tank waste samples have some divalent and trivalent anions (sulfate, carbonate, phosphate, and some other trace ions), so the ionic strength will be slightly larger in the real tank waste samples at a given sodium molarity. The (relatively) low solubility of these divalent and trivalent salts limits their concentrations at high sodium concentrations. <sup>[27-29]</sup> The difference between 1/Q for the simple systems and real waste was much larger than the difference between the simple systems as a function of ionic strength over nearly the entire sodium molarity range. Between one and seven molar sodium concentration, the OH:Al ratio only changed about 10% in the Li et al. <sup>[25]</sup> data, but differed by as much as an order of magnitude from the tank waste samples. Thus, the difference between real waste and the simple systems is not solely due to an ionic strength difference at a given sodium molarity (at least between two and seven molar). The Li et al. <sup>[25]</sup> data are actually trending closer to the real waste data at higher sodium molarities (Fig.1). From

the present data, it cannot be determined if the simple system data would trend onto the tank waste data at higher sodium concentrations.

One interesting note is that the OH:Al ratios as a function of sodium molarity were nearly identical in the Li et al.<sup>[25]</sup> and Wesolowski<sup>[16]</sup> studies, even though Wesolowski<sup>[16]</sup> altered the sodium molarity by adding NaCl. The maximum OH<sup>-</sup> molarity in the Wesolowski<sup>[16]</sup> data is 0.1 M, with the rest of the sodium being made up by NaCl. In contrast, OH<sup>-</sup> is the most prevalent Na-charge balancing anion in the Li et al.<sup>[25]</sup> data, with hydroxide concentrations greater than six molar in some cases. Thus, the effect of monovalent sodium-bearing electrolytes on the OH/Al ratio is roughly the same regardless of the anion identity.

Now that it has been established that the apparent aluminum solubility exhibited by tank waste is much higher than in the simple system reported in the literature,<sup>[16, 25]</sup> some explanation is required. Reynolds and Reynolds<sup>[18]</sup> evaluated Barney's<sup>[17]</sup> simulant data and concluded that there are at least two contributing factors to the high solubility observed by Barney. One of those is that the aluminate dimer and the sodium aluminate ion-pair are more prevalent species in the liquid phase Barney<sup>[17]</sup> simulants than the simple system data. They concluded this because Barney's simulants had much lower water content than a simple sodium hydroxide solution of the same free hydroxide concentration, which would favor the formation of these species. It is not clear if this is a major driver in the present study, because the apparent enhanced aluminum solubility was observed even at relatively low sodium molarities (two to four molar Na). In contrast, Barney studied 10.5 to 19 M Na solutions. The aluminate dimer and the sodium-

aluminate ion-pair may be more important for the tank waste samples with the highest sodium molarities.

Reynolds and Reynolds<sup>[18]</sup> also concluded that the Barney<sup>[17]</sup> data was affected by slow kinetics. Barney equilibrated his samples only from the supersaturation direction, and only for seven days. Reynolds and Reynolds<sup>[18]</sup> concluded that Barney's<sup>[17]</sup> studies likely had not reached a true equilibrium point, because seven days was a short time relative to the equilibration times required by other studies in the literature.<sup>[30, 31]</sup> Slow kinetics may affect the current study as well. The time available for equilibration varied widely for the 50 data points used in the present study, ranging from 21 days to 23 years (Table 1). Given that we cannot confirm that all, or any, of the characterization data used in the present study had come to equilibrium, we have chosen to denote  $1/Q$  as the "apparent" equilibrium ratio rather than the true equilibrium value.

One problem with the assumption that slow kinetics account for all of the apparent supersaturation in Figure 1 is that all of the samples above two molar sodium concentrations appear supersaturated. Given the large number of tanks evaluated in this study, it is surprising that they are all supersaturated and none under-saturated when the sodium molarities are above two molar. The effect of tank history on gibbsite supersaturation could not be determined, but there is nothing in the tank history that would suggest that equilibrium would have always come from the supersaturation direction. Thus, it would be surprising if there were no samples below or near saturation if kinetics were the sole reason for the elevated aluminum concentrations observed. Each tank sample has its own unique history. Some of the samples were created by evaporating supernatants, some by blending supernatants; some were created straight from the

process facilities. Most samples are a result of some combination of these three processes.

A more detailed description of tank waste history can be found in Agnew.<sup>[32]</sup>

Agnew<sup>[20]</sup> believed that the apparent supersaturations in tank waste with respect to gibbsite results from the wastes are equilibrated with solid-phase dawsonite instead of gibbsite. This hypothesis does not explain, however, why the liquids are still supersaturated with gibbsite.

Dawsonite is more soluble than gibbsite under most conditions. If the samples are supersaturated with gibbsite, then gibbsite should still precipitate until equilibrium is reached with respect to gibbsite as well as dawsonite. Gibbsite has been identified in many Hanford tanks,<sup>[9]</sup> so it is reasonable to conclude that gibbsite can precipitate from Hanford waste liquids. A possible explanation of the apparent supersaturation of gibbsite is the simultaneous slow precipitation of gibbsite coupled with the slow dissolution of a less stable phase. If the tanks have a less stable phase, like dawsonite, then this less stable phase would slowly dissolve and re-precipitate the more stable phase. If the dissolution of the less stable phase was faster than the precipitation of the more stable phase, the solution would always be supersaturated with the more stable phase, until the less stable phase has been completely consumed. The liquid would be poised at the saturation concentration of the less stable phase until all of the less stable phase was consumed. This, if true in the case of Hanford tank waste, would explain Agnew's<sup>[20]</sup> conclusion that many tanks appear to be near the dawsonite saturation point. The present study cannot confirm this hypothesis. Dawsonite has been observed in some Hanford tank waste samples<sup>[11]</sup> but it is not clear if dawsonite is present in enough tank samples to account for the wide-spread elevated aluminum concentrations observed.

Until it is possible to determine if the large differences in solubility observed are due to kinetic or thermodynamic factors, it is unreasonable to use real tank waste data to validate thermodynamic-based solubility models. This is because a system that is not at equilibrium would be inconsistent with an equilibrium model. Similarly, it may not be appropriate to use a thermodynamic model to predict aluminum solubility if the waste never comes to equilibrium over the time frame of interest. Thus, determining the reason for the elevated aluminum concentrations is important for determining the appropriate way to model aluminum distribution during waste processing.

## CONCLUSION

This study has concluded that Al(III) appears to be more soluble in Hanford waste than would have been expected based on the ionic strength and measured hydroxide concentrations. This conclusion has been determined by comparing real tank waste data to simple system data that has frequently been used as waste analogues. Both thermodynamic and kinetic factors have been discussed to explain this phenomenon, but no conclusions could be made conclusively in this regard with the present data. If real waste samples are to be used to validate Al(III) models, then determining if thermodynamic or kinetic factors are driving the elevated Al(III) concentrations in the tanks sample is of paramount importance. Testing an equilibrium model against data that is not actually at equilibrium would be inappropriate. Furthermore, an equilibrium model may not be an appropriate model to use if the kinetics is so slow that equilibrium is never realistically reached.



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#### FIGURE CAPTIONS

**Figure 1.** OH:Al Mole ratio as a function of sodium Molarity for tank waste and simple systems.

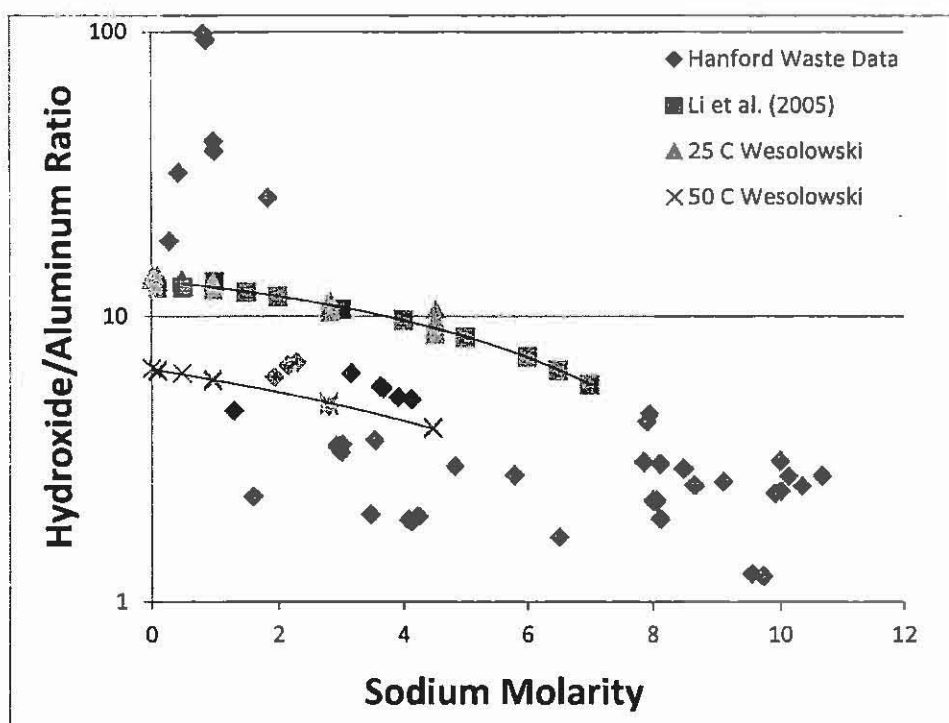


Fig.1

**Table 1.** List of samples investigated in Figure 1, ordered from lowest to highest sodium molarity

Sodium Molarity	OH:Al Mole Ratio (1/Q)	Time Before Last Change to Tank and Sample
0.29	18.30	2 years
0.44	31.84	2 years
0.83	98.67	3 years
0.87	93.24	3 years
0.99	41.18	11 years
1.00	37.94	11 years
1.00	41.07	11 years
1.31	4.66	21 days
1.60	2.34	6 months
1.84	25.94	1 year

Sodium Molarity	OH:Al Mole Ratio (1/Q)	Time Before Last Change to Tank and Sample
1.94	6.12	21 days
2.16	6.72	21 days
2.30	6.89	21 days
2.81	4.84	21 days
2.92	3.50	3 months
2.96	3.43	3 months
3.00	3.34	3 months
3.02	3.55	3 months
3.16	6.31	6 months
3.46	2.02	3 months
3.54	3.66	2 years
3.62	5.68	6 months
3.67	5.59	6 months
3.92	5.21	6 months
4.07	1.94	5 years
4.13	1.91	5 years
4.13	5.12	6 months
4.23	1.99	5 years
4.83	2.98	3 months
5.79	2.77	4 years
6.51	1.68	17 years
7.85	3.08	23 years
7.91	4.27	3 months
7.96	4.54	3 months
8.01	2.26	3 years, 3 months
8.06	2.23	3 years, 3 months
8.07	2.27	3 years, 3 months
8.12	3.04	23 years
8.12	1.94	1 year

Sodium Molarity	OH:Al Mole Ratio (1/Q)	Time Before Last Change to Tank and Sample
8.49	2.92	10 months
8.65	2.55	10 months
9.11	2.63	10 months
9.55	1.25	17 years
9.73	1.23	17 years
9.91	2.40	10 months
10.00	3.11	16 years
10.01	2.44	16 years
10.14	2.75	16 years
10.36	2.54	16 years
10.68	2.76	15 years

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