

Experimental Studies of the Solubilities of Aluminum Oxy-Hydroxy Phases to 300°C

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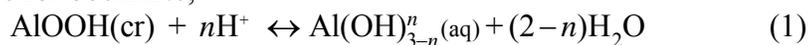
ABSTRACT

The equilibrium solubilities of gibbsite, $\text{Al}(\text{OH})_3$, and boehmite, AlOOH , have been extensively studied in our laboratory from 30 to 90°C, and 100 to 300°C, respectively, to ionic strengths of $5 \text{ mol}\cdot\text{kg}^{-1}$ (NaCl) over a wide range of pH. The resulting solubility constants have been treated with consistent empirical models that incorporate appropriate experimental data taken from the literature. These studies were initiated in part to understand and quantify scale formation in geothermal fields as a result of fluid re-injection from electric power generating plants. Most of the experimental results were obtained through application of a unique potentiometric method that allows for rapid, precise measurement of the *in situ* pH and allows the approach to equilibrium to be monitored from under- and super-saturation. The experimental program was extended to deal with more basic solutions (*e.g.*, five molal NaOH), in which the dissolution of boehmite was measured for application to the refining of bauxite by the Bayer process. More recent results in strong caustic solutions at temperatures below 90°C were obtained to investigate the dissolution of aluminum-containing sludge from holding tanks at the Savannah River waste reprocessing site. In this case the solubility enhancing effects (kinetic and equilibrium) of triethanolamine were also established and quantified. Finally, potentiometric solubility experiments were conducted (50°C in $0.1 \text{ mol}\cdot\text{kg}^{-1}$, NaCl) on aluminum alloy sheets to identify mainly the nature of the aluminum oxide/hydroxide surface layer formed under these conditions.

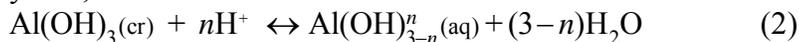
INTRODUCTION

The motivating factor for studying sludges (specifically at the Savannah and Hanford sites) containing high concentrations of sodium hydroxide and nitrate, as well as silica in many cases and other metals and actinides, was to develop a chemical strategy to optimize removal of aluminum. These aluminum phases have been rarely characterized, but are believed to contain substantial quantities of gibbsite and boehmite with varying amounts of bayerite and aluminosilicates, principally hydroxy- and nitrate-sodalites with some cancrinite and zeolite-A. Temperatures range from near ambient to 90°C, which can be attained with *in-situ* heaters and/or may be due to radiation decay. Knowledge of the dissolution rates and equilibrium levels of dissolved aluminum is obviously crucial to optimizing the removal of aluminum from the sludge with respect to time, cost, volume and caustic minimization. Various additives, such as triethanolamine (TEA), were considered as potential solubility-enhancing agents. Moreover, understanding the behavior of aluminum under the above conditions has direct application to bauxite dissolution and the re-precipitation of gibbsite as well as other more unwelcome phases as experienced by the aluminum production industry.

In view of the above description the main focus of this paper is on basic solutions where the aluminate anion, Al(OH)_4^- , is the predominant species in solution. The general solubility equilibria are for boehmite,



and for gibbsite and bayerite,



Bayerite is the least stable phase whereas gibbsite appears to exist metastably with respect to boehmite to *ca.* 80°C almost indefinitely. There are many solubility studies involving aluminum-bearing phases to be found in the literature, although emphasis in this paper is on studies conducted at ORNL. Recently, Bénézeth *et al.* (1) and Palmer *et al.* (2) reported the solubility of boehmite at high temperatures (100 – 300°C) using a unique technique that involved *in situ* measurements of pH over a wide range to high ionic strengths (5 mol·kg⁻¹, NaCl). This technique has the added advantage of obviating the need for pH buffers that had to be employed in many of the previous studies, particularly of gibbsite solubility in our laboratory (3). For the specific case of boehmite in alkaline solutions there is also a more recent study by Panias *et al.* (4). Solubility measurements of gibbsite in caustic media have been reported by Wesolowski (5) and Apps *et al.* (6). Data for bayerite solubility in sodium hydroxide solutions were reported by Fricke (7,8), Hermann and Stipetić (9), Sato (10), Russell *et al.* (11), Chistyakova (12), Apps *et al.*, (6) and Verdes *et al.* (13). Despite the numerous investigations of the solubility of aluminum-bearing solid phases in basic media, the reported solubility constants ($n = 4$) differ considerably. The thermodynamic quantity, K_{s4} , at infinite dilution corresponding to equilibria (1) and (2) expressed for convenience in the basic form is defined by:

$$\log_{10} K_{s4} = \log_{10} \left(m_{\text{Al(OH)}_4^-} \gamma_{\text{Al(OH)}_4^-} \right) - \log_{10} \left(m_{\text{OH}^-} \gamma_{\text{OH}^-} \right) \quad (3)$$

whereas the corresponding molal concentration quotient (or molal solubility quotient), Q_{s4} , at a given finite ionic strength is defined by:

$$\log_{10} Q_{s4} = \log_{10} \left(m_{\text{Al(OH)}_4^-} \right) - \log_{10} \left(m_{\text{OH}^-} \right) \quad (4)$$

Disparities exist not only in the experimental equilibrium values, but also in the mathematical treatments used to calculate the molal solubility constant, *i.e.*, the choice of activity coefficient model. Pitzer (14) improved the semi-empirical approach by extending the Debye-Hückel limiting law to high ionic strengths. The Pitzer ion interaction equation has proven its ability to describe accurately electrolyte behavior in aqueous systems containing high concentrations of NaAlOH₄, NaOH and NaCl, (5,15). The Gibbs energy of formation of the aluminate ion is well known, as are the thermodynamic properties of gibbsite at 25°C (5,16). The corresponding data for the metastable phase, bayerite, are not well quantified, so application of the Pitzer treatment to all the aqueous aluminum species in common in both the gibbsite and bayerite systems will lead to a better, and more consistent, set of thermodynamic data for bayerite as well.

EXPERIMENTAL DETAILS

Gibbsite used in this study was obtained from ALCOA (composition C-33). The raw product was treated by acid washing, followed by rinsing with deionized water for seven days (5). Boehmite (AlOOH) was synthesized hydrothermally at 200°C from the pure gibbsite using a procedure given by Bénézech *et al.* (17). The synthesis of bayerite was based on dissolution of aluminum powder in caustic solution (6 mol·dm⁻³) with a mole ratio, [OH]/[Al], of eight at 0°C. A stream of CO₂ gas was then used to precipitate the bayerite crystals, which were washed repeatedly with deionized water. The sodalites were also prepared hydrothermally. Aluminum sheets (alloy 3104 “can body stock” supplied “as rolled”) were obtained courtesy of ALCAN and were cleaned by submerging in hexane for several days, then rinsing with acetone, washing thoroughly with deionized water. The clean sheets were finally dried in a vacuum oven where they were stored until used.

All of the solid phases and the aluminum sheets were characterized by XRD, SEM and BET before and after the experiments in order to assure the purity and crystallinity of the solids. Raman spectroscopy and NMR were also used to identify the oxyhydrates of aluminum. The surface areas of boehmite, gibbsite and bayerite were initially 2.2, 0.36 and 5.2 m²·g⁻¹, respectively.

Batch experiments at 30 and 63°C were conducted for the solubility measurements in strong caustic solutions. The solid/solution mixtures were contained in sterilized 20 or 50 cm³ disposable polypropylene/polyethylene syringes mounted on a rotating rack submerged in a water bath. The weight ratio of solid to solution was initially 1.2/50 but increased during each experiment as a result of sampling the solution. At 90°C, Savilex (PTFA) 30 cm³ containers fitted with silicone laminates (septa), which allow sampling of the solution with a syringe were used inside a forced-convection air oven. Due to the fast

dissolution kinetics at this temperature, even for the boehmite, no agitation was necessary. Temperature was generally controlled to within $\pm 0.1^\circ\text{C}$. At each temperature, aliquots of about 1-2 g of solution were forced through a $0.2\ \mu\text{m}$ fluorocarbon filter medium (Gelman Laboratory) and immediately diluted with a $0.2\ \text{mol}\cdot\text{kg}^{-1}$ HNO_3 solution to prevent re-precipitation. The aluminum analyses were performed by ICP-AES, which has a linear response over the range from 2 to 200 ppm.

The experiments designed to monitor the solution chemistry resulting from the interaction of the rolled aluminum sheet under dilute acidic to dilute basic conditions ($I = 0.1\ \text{mol}\cdot\text{kg}^{-1}$, NaCl) at 50°C were performed in a hydrogen-electrode concentration cell (or HECC) (2). The presence of excess salt is required in this cell to minimize activity coefficients differences between the test and reference compartments of the cell and to minimize the liquid junction effects. A rolled aluminum sheet coupon of about $600\ \text{cm}^2$ ($\sim 0.120\ \text{m}^2\cdot\text{g}^{-1}$) was placed in the test compartment of the cell in contact with *ca.* 400 mL of test solution and the pH_m ($= \log m_{\text{H}^+}$) was monitored continuously; solution samples were withdrawn periodically for analysis of the aluminum and magnesium content, and either basic or acidic titrant was added incrementally after the pH_m and aluminum concentration stabilized.

DISCUSSION

The following discussion focuses mainly on new solubility experiments conducted in our laboratory on the solubilities of gibbsite, boehmite, bayerite and the aluminum can body stock. These new data will be referenced to experimental results obtained previously at ORNL and elsewhere with the discussion broken down into subsections that deal briefly with each aspect of aqueous aluminum chemistry that has been addressed in our laboratories. In order to lay the groundwork for the subsequent discussion a typical solubility profile for boehmite is shown in Figure 1. These results were obtained from three independent titrations of boehmite in the HECC using both acidic and basic titrants to change the pH with the consequence that the solubility equilibrium was approached from both under- and super-saturation, thereby establishing that equilibrium was truly reached. The solubility quotients for four dissolved aluminum species ($n = 3, 1, 0$ and -1 , Eq. 2) could be extracted from these results. The Q_{s1} value corresponding to the formation of $\text{Al}(\text{OH})^+$ was determined previously from potentiometric titrations of homogeneous aluminum solutions (18) and was required as the stability of this “minor” species could not be extracted unambiguously from the solubility data, despite the large number of experimental results obtained. From a series of similar measurements made from 100 to 290°C at 0.03 to $5.0\ \text{mol}\cdot\text{kg}^{-1}$ ionic strengths, a matrix of solubility quotients was formed, so that each quotient could be fitted by an equation which incorporated the appropriate Debye-Hückel term and a minimal number of temperature and additional ionic strength terms.

For gibbsite the database is more limited, except for studies conducted in basic solutions. For bayerite there are still fewer published results available.

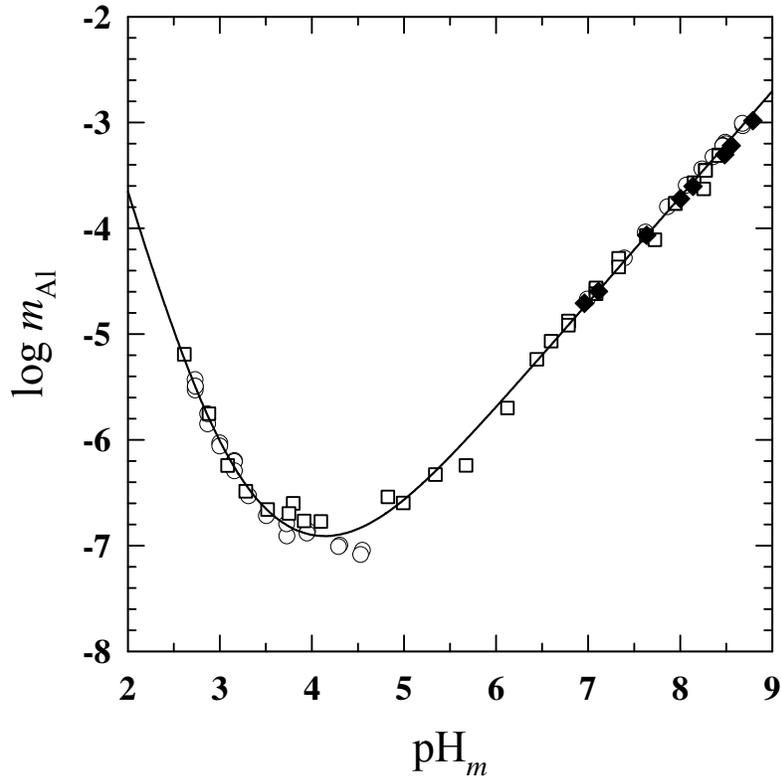


Figure 1 – Solubility of boehmite at 152.4°C in 0.1 mol·kg⁻¹ ionic strength (NaCl) solution based on three titrations in the HECC. The solid curve results from the fit of the isothermal data with $Q_{1,1}$ fixed at a value taken from Palmer and Wesolowski (18). This figure was taken from Palmer *et al.* (2).

Equilibrium Solubility in NaNO₃/NaOH Media

These measurements involved the dissolution of gibbsite, bayerite and boehmite at 0.1 to 5 mol·kg⁻¹ ionic strength (mainly made up of NaNO₃ and NaOH to reflect the composition in the waste storage tanks at the Savannah River and Hanford sites) in the range 30 to 90°C with a more limited number of experiments involving sodalites of hydroxide, nitrate and chloride. Equilibrium with respect to boehmite was not achieved by the batch technique even after many months of equilibration, except at 90°C. Figure 2 shows the results for the other two principal solids, gibbsite and bayerite.

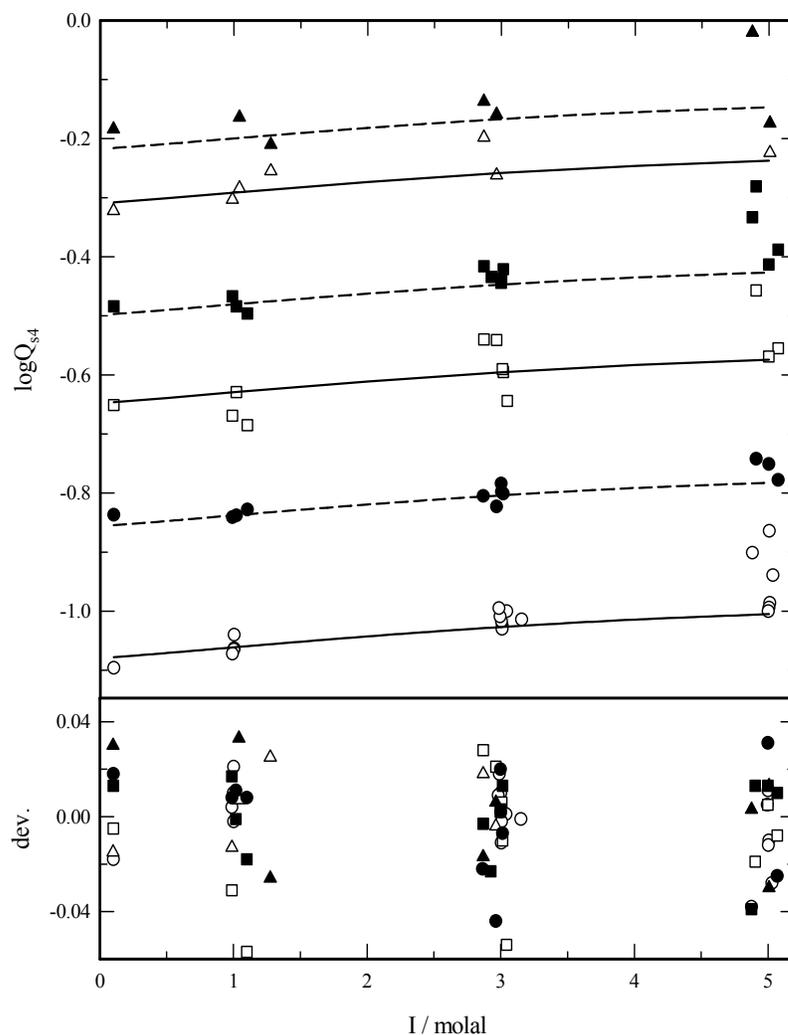


Figure 2: $\log Q_{s4}$ versus ionic strength for bayerite (filled symbols) and gibbsite (open symbols): \bullet, \circ , 30.0°C; \blacksquare, \square , 63.0°C; $\blacktriangle, \triangle$, 89.8°C. The curves were derived from a Pitzer treatment (14) for an initial NaOH concentration of 0.1 mol·kg⁻¹. The deviation between the experimental data and predicted quotients is shown in the lower plot.

Wesolowski (5) measured the dissolution and precipitation of gibbsite in the aqueous system, NaAl(OH)₄, NaOH and NaCl, and these results are in good agreement with the present results in pure NaOH solutions. Apps *et al.* (6) reviewed the available information on bayerite dissolution in the range 0-100°C. Although a discussion of the Pitzer treatment is beyond the scope of this report, a few observations or comments are called for. Note that the data sets for both gibbsite and bayerite were treated simultaneously as the solutions parameters should be consistent. Comparison of the data

for NaCl and NaNO₃ media showed that $\Theta_{\text{Al(OH)}_4\text{-X}}$ and $\Psi_{\text{Na-NaAl(OH)}_4\text{-X}}$ (X = Cl or NO₃) do not differ significantly within our ability to calculate these relatively minor contributions to the overall Gibbs energy of the reactions. The treatment underestimates the experimental solubility quotients obtained by Lyapunov *et al.* (19) and Russell *et al.* (11). The latter authors reported the solubility of β -aluminum-trihydrate, which was presumed to be bayerite. However, interpretation of previous studies is difficult, because bayerite is known for its instability with respect to gibbsite (8,10). It is immediately apparent from Figure 2 that bayerite exhibits a higher solubility quotient than gibbsite with this difference becoming greater with decreasing temperature.

Subsequently, the common Pitzer parameters derived for gibbsite/bayerite were applied to predict boehmite solubility using the five temperature dependent terms for $\log K_{s4}$ proposed by Palmer *et al.* (2). The results of this equation agree with the eleven experimental $\log K_{s4}$ values obtained in our study of boehmite solubility at 90°C to within ± 0.03 log units. The data from Russell *et al.* (11) between 80-100°C are underestimated by an average of ± 0.19 log units although better agreement was obtained with the more recent work of Panias *et al.* (4). The latter authors included an equation for boehmite solubility valid from 30 to 150°C. The difference between the Pitzer treatment developed in the present study and the empirical equation formulated by Panias *et al.* (4) is within ± 0.06 in log units at temperatures < 100°C.

The calculated $\log K_{s4}$ values for the gibbsite and boehmite indicate that the transition temperature for conversion of gibbsite to boehmite is close to 25°C. The conversion must be sufficiently slow to allow gibbsite to exist as a metastable phase at temperatures < 80°C for long periods of time.

The obvious conclusions from the perspective of equilibrium thermodynamics are that higher hydroxide concentrations and higher temperatures strongly favor dissolution of aluminum oxy-hydroxide phases from the sludge piles with the nuclear waste storage tanks.

Kinetics of Dissolution in NaNO₃/NaOH Media

The rates of dissolution of the aluminum-bearing solid phases investigated here are dependent on the specific surface area of the solid, pH, ionic strength and saturation index. In the batch experiments at 30°C, equilibrium solubility with respect to gibbsite dissolution was reached after 7 and 20 days at 1 and 5 mol·kg⁻¹ NaOH, respectively. Bayerite dissolution was complete within 4 days at these conditions. At 63 and 90°C, dissolution was so fast (less than one day) that the difference in the relative rates could not be quantified. Certainly, decreasing the initial NaOH concentration or increasing the ionic strength caused a marked reduction in the rate of dissolution.

Boehmite dissolution is known to be a much slower process (4,5,11). At 90°C, equilibrium values were attained in 1 and 5 mol·kg⁻¹ NaOH after 18 and 35 days,

respectively, whereas at 63°C, equilibrium was reached after 100 days in 1 molal NaOH (no added NaNO₃), whereas in 5 mol·kg⁻¹ NaOH it was not attained even after 200 days.

The kinetic database is too large to be discussed in detail here and therefore only the general aspects of the kinetic behavior are illustrated below. The first deals with the effect of ionic strength on the rate of dissolution that is more readily seen in Fig. 3 for the less labile boehmite. These experiments were carried out at 30°C in varying total (NaNO₃) solutions containing 1 mol·kg⁻¹ NaOH and they demonstrate that the rate of dissolution decreases with increasing ionic strength. At constant caustic concentration, the rate of dissolution decreases with increasing ionic strength. Interestingly, in strongly acidic solutions, the reverse situation occurs.

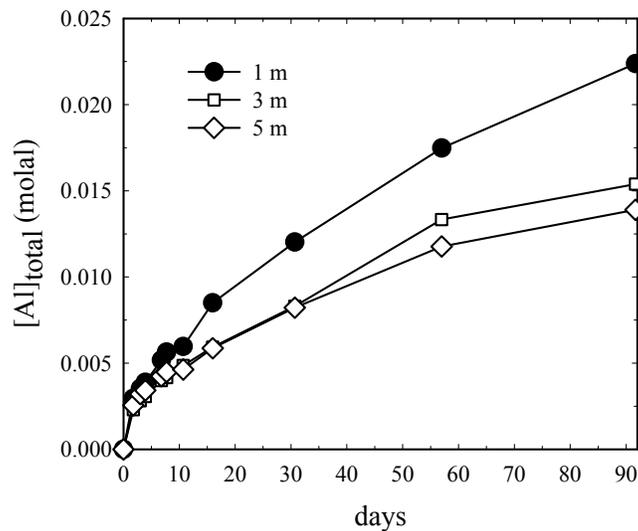


Figure 3 - The effect of ionic strength (NaNO₃) on the dissolution kinetics of boehmite at 30°C in solutions containing 1.0 mol·kg⁻¹ NaOH.

Figure 4 illustrates the effect of increasing the caustic concentration at a constant ionic strength of 3.0 mol·kg⁻¹ on the dissolution kinetics of boehmite. The interesting feature is that in terms of the degree of under-saturation of aluminum, for the lowest hydroxide concentration, the equilibrium solubility is approached after several days compared to the highest concentration of hydroxide where the solutions are still severely under-saturated after 3 months at 30°C. Therefore, whereas as high temperatures and high caustic concentrations will promote dissolution of aluminum containing phases, economics may under some circumstances favor lower temperatures, larger volumes of more dilute NaOH with low concentrations of other salts present.

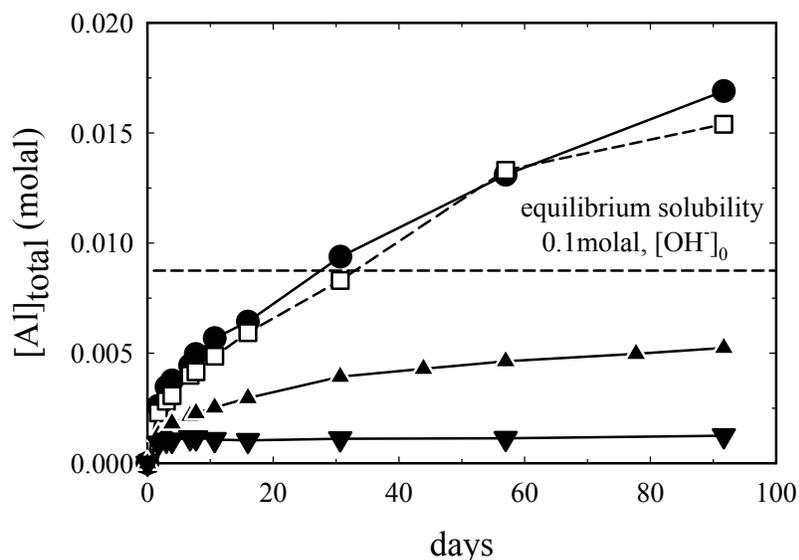


Figure 4 – The effect of varying the hydroxide concentration on the dissolution kinetics of boehmite at 30°C in 3.0 mol·kg⁻¹ ionic strength (NaNO₃) solutions.

Effect of Additives on the Dissolution Rates and Equilibrium Solubilities of Aluminum-Bearing Phases.

The following compounds were tested to determine their effects on the dissolution of gibbsite, bayerite and boehmite: N-methyldiethanolamine, diethanolamine, poly-acrylic acid (two molecular weight fractions), sodium gluconate, triethanolamine (TEA) and bis(2-hydroxyethyl)-tris(hydroxymethyl)methane (Bis-Tris). The first three compounds had no discernable effect on either the kinetics of dissolution or the final solubility. Sodium gluconate inhibited the rate of dissolution, whereas the latter two compounds enhanced the dissolution process substantially. Raman and NMR evidence suggest the existence of unique complexes between the aluminate anion, and TEA and Bis-Tris. NMR and ion-exchange results indicate that the equilibrium involved in the formation of complexes between aluminate and TEA is as follows:



For gibbsite, which dissolves rapidly at low temperatures in the absence of TEA, Fig. 5 demonstrates that increasing temperature destabilizes the Al(OH)_4^- -TEA complex so that the strongest effect on the equilibrium solubility was observed at 30°C. However, its decreasing effectiveness with increasing temperature could be offset by economic and disposal issues that of course are always considerations when choosing the method of removing metals from such sludge piles.

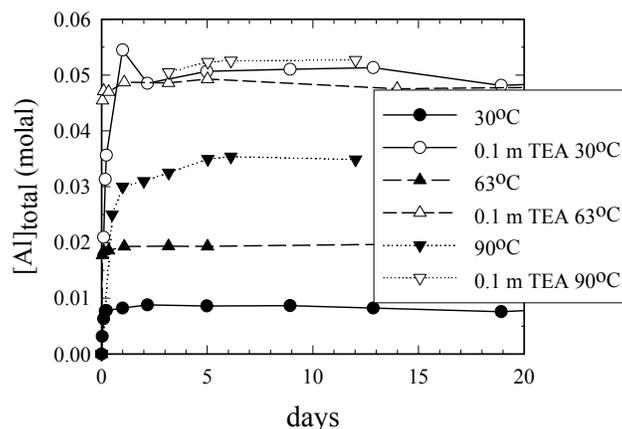


Figure 5 - The effect of TEA on the solubility of gibbsite in $0.1 \text{ mol} \cdot \text{kg}^{-1}$ NaOH (3 molal ionic strength, NaNO_3) as a function of time.

The effect of increasing the concentration of TEA on the rate of boehmite dissolution is illustrated in Fig. 6. The rates are still very slow at low temperatures. The factors that enhance the rate of dissolution of boehmite are: lower ionic strength, higher temperatures, higher TEA concentrations, and higher hydroxide concentration to the limit of about one molal, above which the rate of dissolution tends to decrease, even when the ionic strength is maintained constant by addition of NaNO_3 .

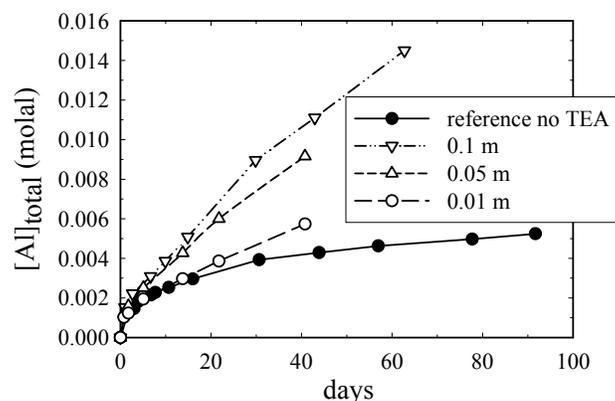


Figure 6 - Influence of varying the TEA concentration on boehmite dissolution at 30°C in $0.1 \text{ mol} \cdot \text{kg}^{-1}$ NaOH (3 molal ionic strength, NaNO_3).

The effect of added TEA on the solubility of hydroxy-, nitrate- and chloro-sodalites was also investigated. Figure 7 shows the dissolution of hydroxy-sodalite as a function of time in terms of the release of aluminum and silica. At 30°C , the maximum solubility is reached within one day, requiring only hours at 63°C . The presence of 0.1 molal TEA has the greatest effect on the release of aluminum at low temperatures (*e.g.*, a four-fold increase even in the presence of $0.5 \text{ mol} \cdot \text{kg}^{-1}$ NaOH at 30°C is shown in Fig. 7). The silica concentration is also enhanced by the presence of TEA, presumably due to the breakdown of the sodalite structure associated with the removal of aluminum ions. The

ratio of Al:Si was observed to be 2.4:1.0 in the original solid (determined by completely dissolving a known mass of sodalite in caustic and analyzing the resulting solution) and this ratio was preserved in the dissolution experiments exemplified in Fig. 7.

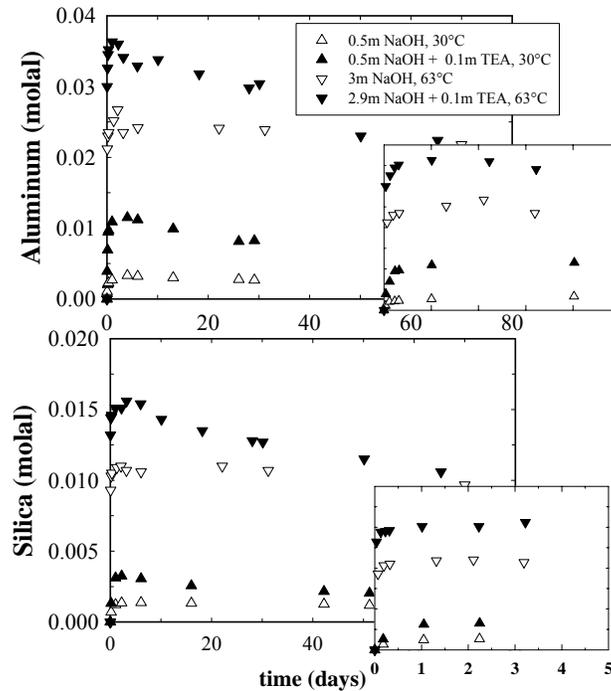


Figure 7: Results of solubility experiments with hydroxysodalite in $3 \text{ mol}\cdot\text{kg}^{-1} \text{ NaNO}_3$ at 30 and 63°C showing the changes in aluminum and silica concentrations with time in the absence and presence of $0.1 \text{ mol}\cdot\text{kg}^{-1} \text{ TEA}$ over an 80-day period. The inserts depict the changes over the initial five days.

The solid phases recovered from these experiments gave XRD patterns consistent with pure hydroxy-sodalite when no TEA was present and a BET surface area that changed from 3.1 to $5.2 \text{ m}^2\cdot\text{g}^{-1}$ after the experiment was terminated. However, in the presence of TEA the surface area increased to $9.9 \text{ m}^2\cdot\text{g}^{-1}$ and a zeolite phase was formed. The presence of this second phase was confirmed by SEM analyses. The SEM images showed clearly that dissolution of the cubic sodalite crystals occurred preferentially at the edges of the cubes and the zeolite formed as balls of tiny platelets. Note that the TEA solutions may have become rapidly over-saturated with respect to SiO_2 accounting at least in part for the subsequent decrease in the silica concentration shown in Fig. 7. However, this precipitate was presumably either a minor component ($< 5\%$) or amorphous because no XRD pattern for this phase was observed. In the absence of TEA, dissolution of the nitrate-sodalite resulted in the formation of cancrinite, whereas under similar conditions the chloro- and hydroxy-sodalites dissolved without the formation of another phase.

The effect of TEA in enhancing the dissolution of sodalites may have application in the descaling of pipes and tanks that are coated with aluminosilicate deposits at waste

treatment sites, geothermal wells, or industrial processing plants. This application would apply particularly to pipes and tanks that could not be easily heated. Finally the solubilities of other metals such as nickel(II) and copper(II), and some actinides are strongly enhanced by the presence of TEA.

Formation of Oxide Layers on Aluminum Sheet exposed to Alkaline Solutions

As a brief background to this section of the paper it is known that the ability to control the surface quality of rolled aluminum sheet is essential to promote aluminum as an industrial material of choice. In most applications, the characteristics of the rolled surface are dependent upon the subsequent coating process. In turn, the coating process is extremely sensitive to the number and nature of surface hydroxyl groups of the aluminum oxides (passivation film) formed on the surface of the sheet. The nature of the oxides varies according to the environment in which it forms (*i.e.*, temperature, oxygen content, pH of the solution in contact with the sheet, *etc.*). This film is normally amorphous. However, under certain and somewhat contentious circumstances bayerite, boehmite, gamma alumina ($\gamma\text{-Al}_2\text{O}_3$), and corundum ($\alpha\text{-Al}_2\text{O}_3$) are found in the passivating layers on aluminum.

Three titration experiments were performed at 50°C in the HECC of strips of the clean aluminum sheet submerged in 0.1 mol·kg⁻¹ NaCl. The pH_m was monitored continuously and periodically solution samples were withdrawn and the total aluminum and magnesium concentrations were determined by ICP-AE. Upon completion of each experiment, the sheet strips were carefully removed from the cell, washed with water and dried under vacuum then submitted to analysis by XRD, SEM and Raman spectroscopy.

Surprisingly, the results of all three titrations that are shown in Fig. 8 indicate that an aluminum phase was formed very rapidly on the surface of the sheet that was stable with time (weeks) and yielded a solubility profile that was very similar to that exhibited by bayerite. Moreover, the XRD pattern of the “oxide” layer on the sheets recovered from the experiments showed sharp peaks consistent with pure, crystalline bayerite. SEM images established that the bayerite formed crystalline columns that completely covered the metal surface. Although the second and third titrations were begun in dilute acidic solutions, overnight the pH_m became basic (see the two arrows in Fig. 8) and further addition of acid caused only a brief lowering of the pH followed by an increase and return to the bayerite solubility curve which corresponds to $\text{Al}(\text{OH})_4^-$ as the dominant form of dissolved aluminum. This behavior was rationalized in terms of the hydrolysis of traces of Mg^{2+} ions released from the surface of the alloy, although the concentration of magnesium did not approach the solubility limit of brucite, $\text{Mg}(\text{OH})_2$. These preliminary results have application in the pretreatment or cleaning of aluminum sheets in industry, and indicate the need for more research to quantify the effects of the resulting surface chemistry caused by changes in the time of exposure, pH, temperature and the presence of additives to the “cleaning” solutions, as well as to the specific composition of the alloy in question.

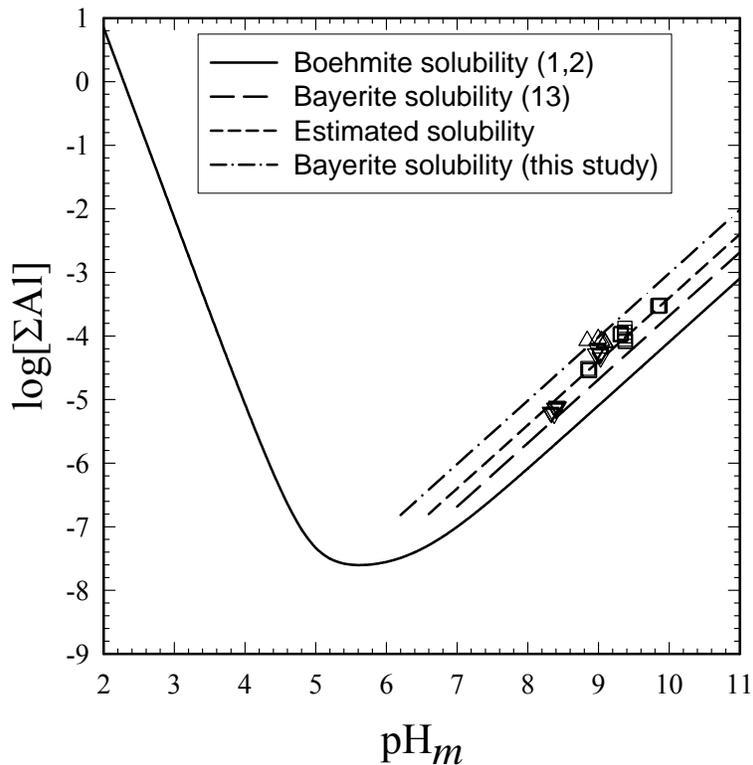


Figure 8 – Plot of the logarithm of the total measured aluminum in solution ($\text{mol}\cdot\text{kg}^{-1}$) versus the measured pH_m showing the data points from three independent titration experiments carried out at 50°C and an ionic strength of $0.1 \text{ mol}\cdot\text{kg}^{-1}$. The curves represent the equilibrium solubility of boehmite and two bayerite phases with the fourth curve representing a linear fit to the present data, imposing a slope of unity.

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