

EXPERIMENTAL STUDY OF THE DISSOLUTION OF ALUMINUM PHASES AS A FUNCTION OF TEMPERATURE, CAUSTIC CONCENTRATION AND ADDITIVES

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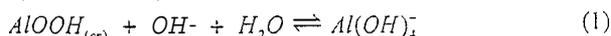
Abstract

The kinetics of dissolution and the equilibrium solubilities of gibbsite, boehmite, bayerite and various sodalites were studied recently in our laboratory from 30 to 90°C as functions of caustic concentration and ionic strength (sodium nitrate) in the absence and presence of triethanolamine (TEA) and other additives. These results build on our existing experimental database of boehmite solubilities to 300°C and gibbsite solubilities to 80°C in sodium chloride solutions. The solubility constants were treated with consistent models that include appropriate experimental data taken from the literature for prediction of solubilities over a wide range of state conditions. The solubility enhancing effect (kinetic and equilibrium) of TEA were also established and quantified. Examples are given of application of a unique potentiometric method that allows for rapid, precise measurement of the approach to equilibrium from under- and super-saturation.

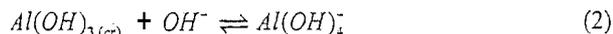
Introduction

The motivating factor for carrying out this new study was to facilitate the dissolution of aluminum from the sludge piles in the holding tanks of the US Department of Energy nuclear waste processing sites at Savannah and Hanford in the United States. These sludges are highly caustic and contain high concentrations of sodium nitrate, as well as silica in many cases and other metals and actinides. The aluminum phases are 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 the key to optimizing the removal of the sludge with respect to time, cost, volume and caustic minimization. Various additives, such as TEA, were considered in this research 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 and other more unwelcome phases as experienced by the aluminum production industry.

In view of the above description and for relevance to raw material processing by the aluminum industry, the main focus of this paper will be placed on basic solutions where the aluminate anion is the predominant species in solution. The pertinent solubility equilibria are, for boehmite,



and for gibbsite and bayerite,



A large number of solubility studies involving aluminum-bearing phases exposed to caustic solutions can be found in the literature. Recently, from this laboratory Benezeth *et al.* (1) and Palmer *et al.* (2) reported the solubility of boehmite at high temperatures (100 – 300°C). There is also a more recent study by Panias *et al.* (3). Solubility measurements of gibbsite in caustic media have been treated by Wesolowski (4) and Apps *et al.* (5). Data for bayerite solubility in sodium hydroxide solutions are reported by Fricke (6,7), Herniann and Stipetić (8), Sato (9), Russell *et al.* (10), Chistyakova (11), Apps *et al.* (5) and Verdes *et al.*, (12). Despite the numerous investigations of the solubility of aluminum-bearing solid phases in basic media, the reported solubility constant values, K_{s4} , differ considerably. The thermodynamic quantity K_{s4} at infinite dilution is defined by:

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

whereas the molal concentration quotient (or molal solubility quotient) Q_{s4} is defined by:

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

Disparities exist not only in the experimental equilibrium values, but also in the mathematical treatments used to calculate the molal solubility quotient. Panias *et al.* (3) used a simple mathematical formalism for modeling activity coefficients of the charged species involved in the dissolution reaction of boehmite (Eq. 1). The activity coefficients were obtained by developing semi-empirical equations given by Meissner *et al.* (13), based on the simple case of sodium chloride. Unfortunately, this model does not approximate the ionic electrostatic interactions at high ionic strength. The limitation of this assessment is even more dramatic at high temperature where the electrostatic forces become stronger and differ from one ion pair to another. An empirical equation has been developed by Palmer *et al.* (2) on the basis of an extended Debye-Huckel term and a number of variable temperature and ionic strength dependent terms. This treatment has been tested in the aqueous system, NaAl(OH)₄, NaOH and NaCl, derived from boehmite dissolution and applies strictly to the measured temperature range of 100 to 300°C, although by incorporating the Gibbs energy of the transformation of boehmite to gibbsite, this treatment should also approximate boehmite dissolution equilibria to ambient conditions, where boehmite remains the thermodynamically stable phase according to this study.

Pitzer (14) has improved the semi-empirical approach by extending the limiting law of Debye-Huckel to high ionic strengths. The Pitzer ion interaction equation has proven its ability to describe accurately electrolyte behavior in the aqueous system containing high concentration of NaAlO₄, NaOH and NaCl, (4, 15). Therefore, this approach was chosen to model the solubility quotients obtained in this study. The Gibbs energy of formation of the aluminate ion is well defined, as is the thermodynamic

properties of gibbsite at 25°C (4,16). The corresponding data for the metastable phase, bayerite, are not well quantified, so application of the Pitzer treatment to 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 Methods

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 (4). Boehmite (AlOOH) was synthesized hydrothermally at 200°C from the pure gibbsite using a procedure given by Bénézeth *et al.* (17). The synthesis of bayerite was based on dissolution of aluminum powder in caustic solution (6M) with a molal ratio of $[\text{OH}]/[\text{Al}]=8$ at 0°C. A stream of CO_2 gas was then used to precipitate the bayerite crystals, which were washed repeatedly with deionized water. The sodalites were also prepared hydrothermally.

All of the solid phases were characterized by X-ray diffraction, 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 (18), and in particular, bayerite after each step of its synthesis (19). The surface areas of boehmite, gibbsite and bayerite were initially 2.2, 0.36 and 5.2 $\text{m}^2 \cdot \text{g}^{-1}$, respectively.

The batch experiments at 30 and 63°C were conducted in sterilized 20 or 50 cm^3 disposable polypropylene/polyethylene syringes mounted on a rotating rack submerged inside 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 cm^3 containers fitted with silicone laminates (septa) that allow sampling of the solution with a syringe fitted with a stainless steel needle 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 1-2g of solution were forced through a 0.2 μm fluorocarbon filter medium (Gelman Laboratory) and immediately diluted with a 0.2 molal HNO_3 solution to prevent precipitation. The aluminum analyses were performed by ICP-AES, which has a linear response over the range from 2 to 200 ppb

Discussion

The following discussion focuses mainly on new solubility experiments conducted in our laboratory on the solubilities of gibbsite, bayerite and boehmite. These new data will be referenced to experimental results obtained previously at ORNL and elsewhere with the discussion broken down into sub-sections that deal briefly with each aspect of aqueous aluminum chemistry that has been addressed in our laboratories.

Equilibrium Solubility in $\text{NaNO}_3/\text{NaOH}$ Media

New experimental measurements involving the dissolution of gibbsite, bayerite and boehmite were performed at 0.1 to 5 molal

ionic strength in the range 30 to 90°C with a 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 1 shows the results for the other two principal solids, gibbsite and bayerite.

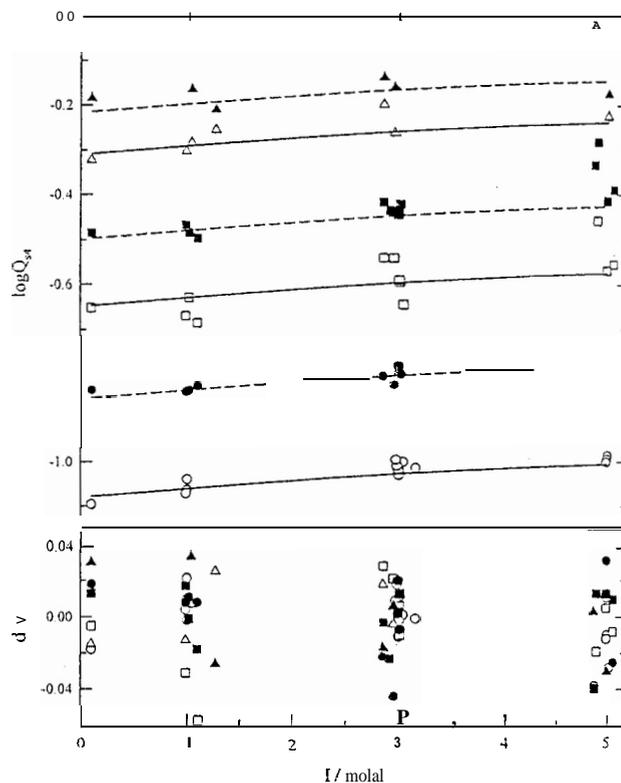


Figure 1: The molal solubility quotient versus ionic strength for bayerite (filled symbols) and gibbsite (open symbols): \bullet, \circ , 30.0°C; \blacksquare, \square , 63.0°C; and $\blacktriangle, \triangle$, 89.8°C. The curves were derived from the Pitzer treatment [14] for the case of an initial NaOH concentration of 0.1 molal. The deviation between the experimental data and predicted quotients is shown in the lower plot with the average standard deviation being ± 0.04 in log units.

Wesolowski (4) measured the dissolution and precipitation of gibbsite in the aqueous system, $\text{NaAl}(\text{OH})_4$, NaOH , and NaCl . Good agreement was apparent between his data and the present results in pure NaOH solutions. Apps *et al.* (5) reviewed the available information on bayerite dissolution in the range 0-100°C. Only a few studies of bayerite exist based on solubility and calorimetric experiments (5,12,20). The thermodynamic properties of bayerite were determined directly from the temperature-dependent expression for $\log K_{s4}$ as described below

The Pitzer ion interaction treatment (14,21) was selected to model the aqueous system, $\text{NaAl}(\text{OH})_4$, NaOH , and NaNO_3 , because it allows the most reliable prediction of solubilities at high ionic strengths and sufficient solubility data are available over a wide range of ionic strength and temperature to allow the many adjustable parameters inherent in this treatment to be extracted

with minimum covariance. The mathematical representation of molal solubility quotient for Eq. (7) is:

$$\log_{10} Q_{s,4} = \log_{10} K_{s,4} - \log_{10} \left(\gamma_{Al(OH)_4^-} / \gamma_{OH^-} \right) \quad (5)$$

The model in terms of individual ions is simplified to:

$$\log Q_{s,4} = -\log K_{s,4} + \frac{1}{2.3026} \times \left[\begin{array}{l} 2[Na^+](\beta_{NaOH}^0 - \beta_{NaAl(OH)_4}^0) \\ + f[Na^+](\beta_{NaOH}^1 - \beta_{NaAl(OH)_4}^1) \\ + I[Na^+](C_{NaOH}^\phi - C_{NaAl(OH)_4}^\phi) \\ + 2\Theta_{Al(OH)_4-OH} ([Al(OH)_4^-] - [OH^-]) \\ + 2[NO_3^-](\Theta_{NO_3-OH} - \Theta_{Al(OH)_4-NO_3}) \\ + [Na^+]\Psi_{Na-Al(OH)_4-OH} ([Al(OH)_4^-] - [OH^-]) \\ + [Na^+][NO_3^-](\Psi_{Na-NO_3-OH} - \Psi_{Na-Al(OH)_4-NO_3}) \end{array} \right] \quad \dots(6)$$

where

$$f = [1 - 2I^{0.5}] \exp(-2I^{0.5}) / I \quad (7)$$

The bracketed terms represent the molal concentrations of each ion, I is the ionic strength, and β^0 , β^1 , C^ϕ represent the pure electrolyte parameters, while Θ and Ψ are the binary and ternary mixing parameters, respectively.

Our approach was to treat the data for bayerite and gibbsite simultaneously in order to produce a consistent fit for the common aqueous species and to extract the best binary and ternary ion mixing parameters involving the aluminate anion.

As these systems contain a single cation (Na^+), the quantity $[Na^+]$ is replaced by the ionic strength. $\log K_{s,4}$ can be expressed in terms of four temperature-dependent terms, so that Eq. 6 can be rewritten by substituting interaction coefficients with adjustable parameters p_1 to p_{15} as shown in Eq. 8. The fit was derived from the 71 values collected in this study and the 14 data points taken from Wesolowski (4), where only values relating to the aqueous system, $NaAl(OH)_4$ and $NaOH$, were considered. Eq. 8 provides a fit of these 85 experimental values to within ± 0.02 in log units.

$$\log Q_{s,4} = -A_G(p_1 + p_2/T + p_3 \ln(T) + p_4 T) - A_B(p_5 + p_6/T + p_7 \ln(T) + p_8 T) + \frac{1}{2.3026} \left[\begin{array}{l} 2I(\beta_{NaOH}^0 - p_9) + fI(\beta_{NaOH}^1 - p_{10}) \\ + I^2(C_{NaOH}^\phi - p_{11}) \\ + 2p_{12}([Al(OH)_4^-] - [OH^-]) \\ + 2[NO_3^-](\Theta_{NO_3-OH} - p_{13}) \\ + Ip_{14}([Al(OH)_4^-] - [OH^-]) \\ + I[NO_3^-](\Psi_{Na-NO_3-OH} - p_{15}) \end{array} \right] \quad \dots(8)$$

A_G and A_B were assigned the values 0 and 1 for G = gibbsite and B = bayerite, respectively, and consequently the parameters p_1 to p_4

and p_5 to p_8 refer to the $\log K_{s,4}$ temperature-dependent parameters for gibbsite and bayerite, where the former were taken from the previous work of Wesolowski (4). Note that the thermodynamic properties derived from the parameters p_1 to p_4 are in good agreement with calorimetric study of Hovey *et al.* (16).

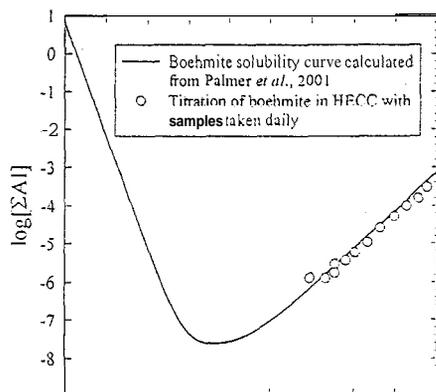
Although the single electrolyte parameters, $\beta_{NaAl(OH)_4}^0$, $\beta_{NaAl(OH)_4}^1$ and $C_{NaAl(OH)_4}^\phi$ are in good agreement with those obtained by Wesolowski (4), the values of binary and ternary mixing parameters from aluminate and hydroxide anions differ, because the previous treatment (4) ignored interactions involving chloride ions. Comparison of the data for $NaCl$ and $NaNO_3$ media showed that $\Theta_{Al(OH)_4-X}$ and $\Psi_{Na-NaAl(OH)_4-X}$ ($X = Cl$ or NO_3) do not differ significantly within the accuracy which is limited by our ability to calculate these relatively minor contributions to the overall Gibbs energy.

The Pitzer treatment underestimates the experimental solubility quotients obtained by Lyapunov *et al.* (20) and Russell *et al.* (10). The latter author 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 (7,9). It is immediately apparent from Figure 1 that bayerite exhibits a higher solubility quotient than gibbsite with this difference becoming greater with decreasing temperature.

Subsequently, Eq. 8 was applied to predict boehmite solubility by fixing the parameters p_8 - p_{15} to the values obtained above, and applying the temperature function for $\log K_{s,4}$ proposed by Palmer *et al.* (2), which contains p_1 - p_4 and an additional $p_{16}T^2$ term. The results of this equation agree with the eleven experimental $\log K_{s,4}$ values obtained in our study of boehmite solubility to within ± 0.03 log units for the temperatures. The data from Russell *et al.* (10) between 80-100°C are underestimated by an average of ± 0.19 log units with better agreement obtained with the more recent work of Pnias *et al.* (3). This author included an equation for boehmite solubility supposedly valid from 30 to 150°C. The difference between the Pitzer treatment given in this paper and the empirical equation formulated by Pnias *et al.* (3) is evaluated to be within ± 0.06 in log units at temperatures $< 100^\circ C$.

Very recently, solubility measurements were carried out at ORNL with boehmite in 0.1 molal $NaCl$ at 50°C in a hydrogen-electrode concentration cell (HECC), which provides a direct, precise and accurate measurement of pH_m (defined as $-\log[H^+]$ on the molality scale) during the equilibration process as described previously (1,2). The presence of an "inert" electrolyte is required to minimize liquid junction potentials between the two compartments of the cell. Efficient stirring in this cell with no mechanical degradation of the suspended solid promotes rapid equilibration. Figure 2 illustrates that equilibrium was attained with 24 hours with respect to boehmite precipitation onto boehmite seed crystal present, as these data were obtained from daily sampling of the test solution. After each equilibration, acidic titrant was injected to perturb the equilibrium (*i.e.*, create oversaturation with respect to boehmite). These new results confirm the $\log K_{s,4}$ values for boehmite obtained from extrapolation of solubility data (solid curve in Figure 2) obtained from 100 to 300°C (2). Moreover, this demonstrates the utility of the HECC for studying the kinetics (see discussion below) and solubility of

aluminum phases at pH_m values up to mildly basic conditions at high ionic strengths.



A comparison of the gibbsite and boehmite $\log K_{s4}$ values determined from Eq. 8 and from Palmer *et al.* (2), respectively, shows that the transition temperature for conversion of gibbsite to boehmite is close to **25°C** indicating that the conversion must be sufficiently slow in that gibbsite can exist as a metastable phase even at 80°C for at least a period of weeks, as shown from the solubility study carried out by Wesolowski (4) at this temperature. This observation is also consistent with the formation of unwanted boehmite following the dissolution of bauxite at low temperatures.

Kinetics of Dissolution in $\text{NaNO}_3/\text{NaOH}$ 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 molal 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 ionic strength reduces markedly the rate of dissolution

Boehmite dissolution is known to be a much slower process (3,4,10). At 90°C, equilibrium values were attained in 1 and 5 molal NaOH after 18 and 35 days, respectively, whereas at 63°C, equilibrium was reached after 100 days in 1 molal NaOH (no added NaNO_3) while in 5 molal NaOH it was not attained even after 200 days. Rate constants have not been extracted from these kinetic data at this time, but qualitative comparisons are made below with the rates obtained in the presence of TEA.

It is relevant to mention in this section our work at higher temperatures with the HECC aimed at establishing the rates of dissolution and precipitation of gibbsite and boehmite in NaCl brines. In Figure 3 is a plot of the logarithm of the aluminum

molality versus pH_m where the experimental equilibrium solubilities (2) are shown in 0.1 molal NaCl at 150°C, as well as the fitted solubility profile (2). The arrows indicate the path of a subsequent experiment where, following additions of acidic then basic titrant, the pH_m was monitored while the system relaxed back to equilibrium solubility with respect to boehmite from super- and under-saturation, respectively. These are virtually isothermal changes that allow the kinetics of these reactions to be followed and each return to equilibrium could be confirmed by analysis of the aluminum content of the test solution. Examples of these kinetic plots will be given in the presentation.

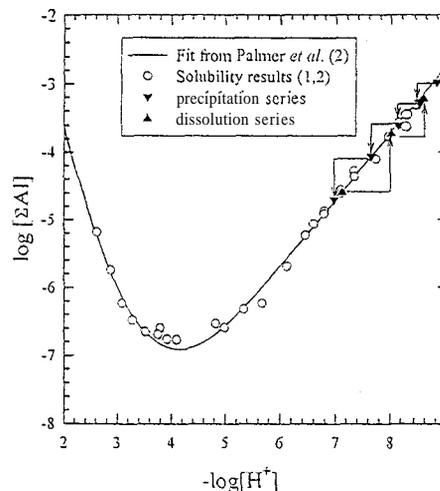
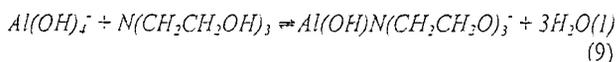


Figure 3: The solubility profile for boehmite at 150°C in 0.1 molal NaCl (2) also showing the results of a subsequent experiment in the HECC where the kinetics of precipitation and dissolution were monitored *in situ* from the change in the measured pH_m .

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 was accumulated for the existence of unique complexes between the aluminate anion, and TEA and Bis-Tris. Earlier work in this laboratory established the formation of this complex involving Bis-Tris, which is a common pH buffer, but the bonding was mistakenly thought to involve two rather than three ethanol groups (22). Independent NMR and ion-exchange evidence suggest that the equilibrium involved in the formation of complexes between aluminate and ETA is as follows:



Some interesting features of the effects of TEA are shown below for each aluminum-bearing solid phase. For gibbsite, which

dissolves rapidly at low temperatures in the absence of TEA, Figure 4 demonstrates that increasing temperature destabilizes the $\text{Al}(\text{OH})_4^-$ -TEA complex so that the strongest effect on the equilibrium solubility was observed at 30°C.

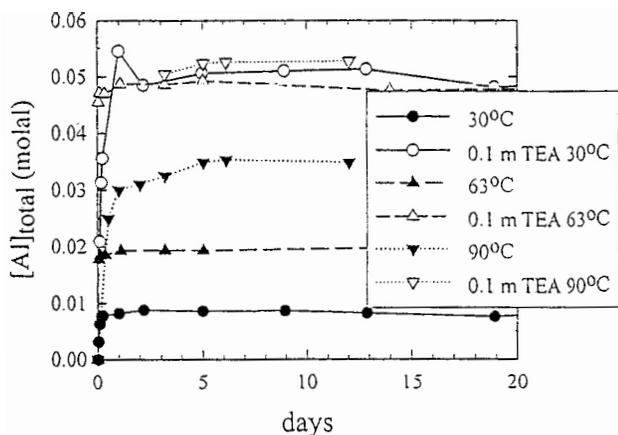
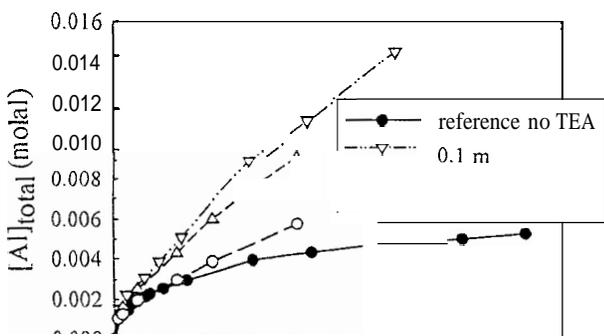


Figure 4: The solubility of gibbsite in 0.1 molal NaOH (3 molal ionic strength, NaNO_3) as a function of time.

The effect of increasing the concentration of TEA on the rate of boehmite dissolution is illustrated in Figure 5. The rates are still very slow at low temperatures. The factors that would enhance the rate of dissolution of boehmite are: lower ionic strength, higher temperatures, higher TEA Concentration, 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 .



silica concentration is also enhanced by the presence of ETA presumably due to the breakdown of the sodalite structure associated with the removal of aluminum atoms. The ratio of Al:Si was determined 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 Figure 6

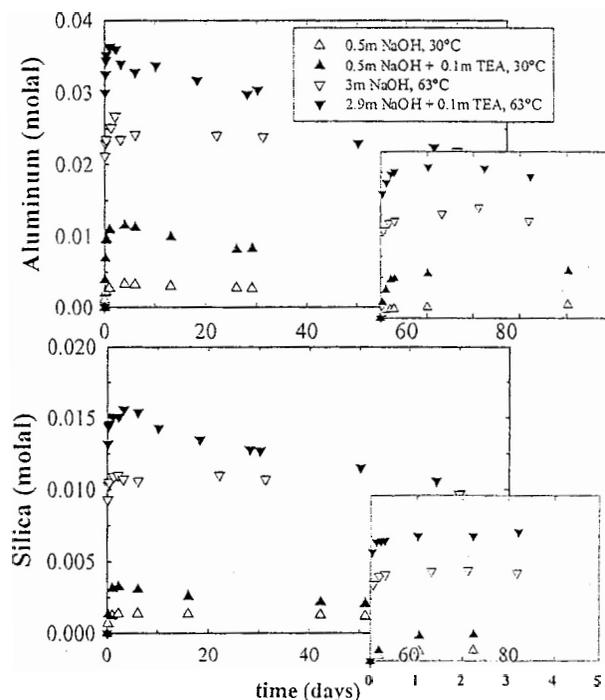


Figure 6: Results of solubility experiments with hydroxysodalite in 3 molal ionic strength (NaNO_3) at 30 and 63°C showing the changes in aluminum and silica concentrations over time in the absence and presence of 0.1 molal TEA over an 80-day period with the inserts depicting the changes over the initial five days.

The solid phases recovered from these experiments gave XRD patterns consistent with pure hydroxy-sodalite when no ETA was present and a BET surface area that changed from $3.1 \text{ m}^2 \cdot \text{g}^{-1}$ to $5.2 \text{ m}^2 \cdot \text{g}^{-1}$ by completion of the experiment. 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 become quickly over-saturated with respect to SiO_2 accounting in part perhaps for the subsequent decrease in the silica concentration shown in Figure 6, but the precipitate was presumably either a minor component (<5%) or amorphous as no XRD pattern for this phase was observed. Interestingly, 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.

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