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THE AQUEOUS CHEMISTRY OF ALUMINUM: A NEW APPROACH TO HIGH TEMPERATURE SOLUBILITY MEASUREMENTS

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ABSTRACT

The solubility of boehmite, AlO(OH) , has been measured as a function of pH (2 - 10, depending on ionic strength), temperature (100 - 250°C) and ionic strength (0.03 - 1 molal, NaCl) in a hydrogen-electrode concentration cell, HECC, which provided *in situ* measurement of hydrogen ion molality. Samples of the solution were withdrawn after the pH reading stabilized for analysis of total aluminum content by ion chromatography. Acidic or basic titrant could then be metered into the cell to affect a change in the pH of the solution. The direction of approach to the equilibrium saturated state could be readily varied to ensure that the system was reversible thermodynamically. This represents our second application of direct pH measurement to high temperature solubility studies. The results at low ionic strength are compared with those from two recently-reported high-temperature studies of boehmite solubility, which relied on the conventional batch technique. Comparisons are also made with the low temperature (<90°C) hydrolysis constants for aluminum garnered from solubility measurements with gibbsite as the stable phase. Based on these preliminary results, it is possible to draw some general conclusions concerning the relative importance of the aluminum species in solution and to reduce significantly the number of experiments needed to define this complex system in a thermodynamic sense.

BACKGROUND

Aluminum is the third most abundant element in the Earth's crust and is a principal component of the common rock-forming minerals (feldspars, micas, amphiboles, epidotes, clays, etc.) in geothermal reservoir rocks and alteration assemblages. Thus, quantitative knowledge of the aqueous speciation and solubility of aluminum ions is critical in modeling

changes in solution chemistry and phase equilibria in geothermal systems, as well as changes in porosity and permeability due to mineral dissolution and precipitation reactions.

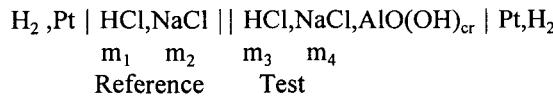
A large disparity has existed in the prediction of the dissolution, transport, and precipitation of aluminum in natural systems based on the sparse experimental data sets reported in the literature (Nordstrom and May, 1989; Verdes, 1990; Bourcier et al., 1993; Castet, et al., 1993; Wesolowski and Palmer, 1994; Anderson, 1995; Pokrovskii and Helgeson, 1995). The estimated solubilities and speciation differed by orders of magnitude, especially when compared to actual field observations where near-neutral solutions abound, corresponding to the minimum in the solubility of these aluminum phases.

A systematic study of the solubility of gibbsite - Al(OH)_3 - in NaCl brines was undertaken in this laboratory over a range of temperatures (0-100°C), pH (2-14), and NaCl concentrations (0-5 mol·kg⁻¹) (Wesolowski, 1992; Palmer and Wesolowski, 1992; Wesolowski and Palmer, 1994). In these experiments the pH was controlled by either the presence of excess acid (or base), or buffering agents, for which independent studies (potentiometry, Raman spectroscopy, and solubility measurements) were performed to quantify their interaction with aluminum in solution (Wesolowski et al., 1989; Palmer and Wesolowski, 1992; Palmer and Bell, 1994). The work reported here obviates the need for the buffers by monitoring pH directly and focuses on the higher temperature regime where boehmite is the most useful working phase, although it is metastable with respect to corundum.

EXPERIMENTAL METHODS

The design and function of the hydrogen-electrode concentration cell (HECC) have been described in numerous publications (e.g., Palmer and Wesolowski, 1992). The present version is larger

than its predecessors and is fitted with sample delivery tubes and functions briefly as follows. The cell consists of a 1 L capacity Hasteloy pressure vessel containing two concentric Teflon cups separated by a porous Teflon plug, which acts as a liquid junction completing the electric circuit. Two Teflon insulated platinum wires coated with platinum black protrude into either cup and serve as electrodes. The solutions in each cup are stirred magnetically. The solution in the inner cup serves as the reference of known hydrogen ion molality, whereas the outer, or test, solution contains a suspension of boehmite (initially ca. 10 g in ca. 400 mL). Both solutions were thoroughly purged with hydrogen at ambient temperature prior to placing the vessel in the tube furnace for equilibration at temperature. Aliquots of the test solution were removed through a platinum dip tube fitted with a condenser via a PEEK® valve and a 0.2 μm filter into a preweighed polypropylene syringe containing a known mass of 1 $\text{mol}\cdot\text{L}^{-1}$ HCl. The initial configuration of the cell in a typical experiment containing identical acidic solutions is as follows:



with the ratios $\text{m}_1:\text{m}_2$ and $\text{m}_3:\text{m}_4$ of <0.1 in order to minimize liquid junction contributions to the measured potential. A primary titrant consisting of NaOH and NaCl at the same ionic strength as the reference and test solutions was employed. A second inert (Zircalloy 700) positive displacement pump cell containing HCl and NaCl at matching ionic strength is connected to the test compartment so that the titration process can be reversed, or initiated in the case where the solubility experiment began on the basic side.

Analyses for aluminum were conducted by ion chromatography (Wesolowski and Palmer, 1994) and on occasion by graphite furnace atomic adsorption.

Boehmite was prepared by hydrothermally treating acid-washed gibbsite (Wesolowski, 1992; Bourcier et al., 1993) at 200°C for two weeks. The crystallinity and surface area of boehmite samples taken before and after a number of solubility experiments were confirmed by X-ray diffraction and SEM. No mechanical degradation of the boehmite was observed as a result of agitation within the cell, in

fact the surface area decreased from 1.95 to 1.73 $\text{m}^2\cdot\text{g}^{-1}$, indicative of particle sizes of 0.4 μm .

RESULTS AND DISCUSSION

Measurement of Hydrogen Ion Molality

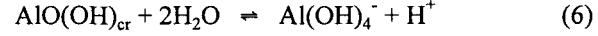
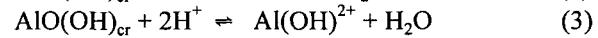
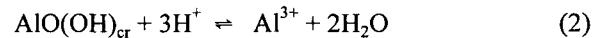
Considering the cell configuration presented above, the desired hydrogen ion concentration in the test compartment of the cell is determined relative to the known concentration in the reference compartment from the Nernst equation:

$$\log m_3 = \log m_1 - F(E + E_{\text{LJ}})/(2.3026RT) \quad (1)$$

where E is the measured cell potential, E_{LJ} is the estimated liquid junction potential (see, Palmer and Wesolowski, 1992), and F , R , and T represent the Faraday constant, the universal gas constant and the temperature in Kelvin, respectively. Numerous experiments have been conducted over the past 25 years confirming that these cells do in fact behave in a strictly Nernstian fashion as dictated by eqn. (1). It is important to stress at this time that the **concentration** of hydrogen ion is measured by this method such that pH is defined as the negative logarithm of the hydrogen ion molality, and **not** by the conventional activity scale. Activity coefficients of H^+ are assumed to be identical in both cell compartments.

Solubility Equilibria

The minimum equilibria that must be considered in elucidating the boehmite solubility results involve monomeric solution species as follows (Bourcier et al., 1993; Castet et al, 1993; Wesolowski and Palmer, 1994):



The equilibrium quotients associated with each of these reactions are defined in general terms as:

$$Q_{\text{1ns}} = [\text{Al(OH)}_n^{3-n}] / [\text{H}^+]^{3-n} \quad (7)$$

where n corresponds to the number of hydroxide ions bound per aluminum in solution, i.e., n varies from 0 to 4 corresponding to eqns. (2) to (6). Ideally, from the dependence of the measured total aluminum as a function of the measured pH the values of each Q_{1ns}

can be extracted, although in practice this is only possible when the species in solution are present to a significant extent, given the accuracy of the measured concentrations. This point is significant and will be elaborated on later in the text.

For comparison with existing data reported at infinite dilution, the activity coefficients of the solution species must be taken into account, such that the thermodynamic equilibrium constant, K_{Ins} , for each reaction is related to the corresponding equilibrium quotient at some finite ionic strength as follows:

$$K_{\text{Ins}} = Q_{\text{Ins}} \gamma_{\text{In}} a_w^{2-n} / \gamma_{\text{H}}^{3-n} \quad (8)$$

where γ_{In} and γ_{H} refer to the activity coefficients of Al(OH)_{3-n} species in solution and hydrogen ion, respectively, and a_w is the activity of water. At low ionic strengths, the ratio of activity coefficients may be modeled after the Debye-Hückel limiting law, whereas at higher ionic strengths it is generally the practice to study the variation in Q_{Ins} at various ionic strengths and fit an empirical equation to these data, incorporating the Debye-Hückel limiting law, for extrapolation to infinite dilution (e.g., Palmer and Wesolowski, 1992).

In the ensuing discussion of the experimental results it must be emphasized that their treatment is preliminary and incomplete as this study is ongoing and the fitting procedure is therefore limited.

Low Ionic Strength Results

In order to compare these new solubility results with those reported in the literature, consider the low ionic strength data ($0.03 \text{ mol}\cdot\text{kg}^{-1}$), which is also virtually the lowest ionic strength practicable with this apparatus in order to keep the liquid junction potential to calculable limits), where the Debye-Hückel expression can be used to approximate the activity coefficients. The lowest temperature studied was 101°C where it is known that boehmite is still the stable phase relative to gibbsite, which nucleates more readily at low temperature. The results of two titrations are shown in Fig. 1, clearly establishing that the data are reproducible. Moreover, equilibrium was established within 12 hours of the system reaching temperature and within eight hours after the addition of titrant. This is about two orders of magnitude faster than reported from conventional batch experiments and is of enormous advantage for the current method, presumably derived from the elevated agitation rate and the higher solid to liquid

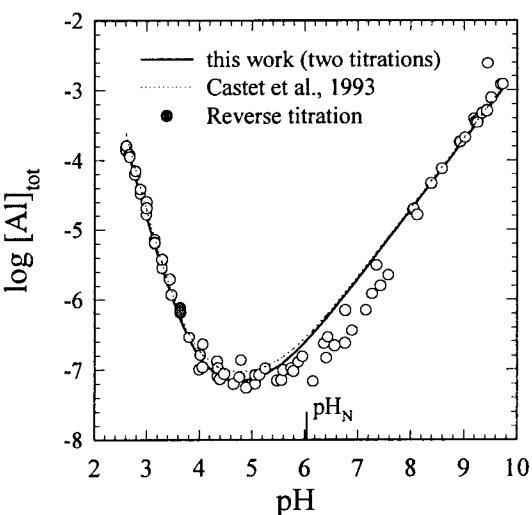


Fig. 1 Solubility profile of boehmite at 101.3°C and $0.03 \text{ mol}\cdot\text{kg}^{-1}$ ionic strength, where pH_N is neutral pH ($= -0.5 \log Q_w$ for water).

ratio employed here. Fast equilibration is important because it ensures that the reference solution remains unaffected with time. The two shaded points in Fig. 1 result from back-titration with the acidic titrant and the observed agreement with the forward titration values establishes that the reference solution composition remained constant. Moreover, it must be remembered that reversing the titration also reverses the approach to equilibrium on both sides of the solubility minimum, further establishing the reversibility of the equilibration.

The agreement between the fitted curves derived from the present study (solid line in Fig. 1) and from the smoothed equilibrium constants reported by Castet et al. (1993) is excellent. The caveat to this comparison is that the K_{Ins} values in the latter study were converted to Q_{Ins} values using the extended Debye-Hückel expression to simulate the activity coefficients appropriate to $0.03 \text{ mol}\cdot\text{kg}^{-1}$ ionic strength, eqn. (8). There is one obvious region of pH values slightly above the solubility minimum in Fig. 1 where the experimental data lie significantly below the solubility curve. This problem is apparent at other conditions and is thought to be due to sluggish kinetics in approaching equilibrium from undersaturation in near neutral solutions. This question is currently under investigation in the laboratory.

A second comparison can be made at 203.3°C including additional data from Bourcier et al. (1993),

who worked in the range of 150 to 250°C. From the results shown in Fig. 2 it is clear that although excellent agreement was found at high pH between the three studies, the discrepancy with the calculated curve based on the smoothed K_{Ins} values of Bourcier et al. (1993) becomes significant at low pH. On the other hand, there is generally good agreement with the Castet et al. (1993) model, with the lower solubility minimum found in the present study being due to the lower predicted stability of the $\text{Al(OH)}_3^{\circ\text{(aq)}}$ species.

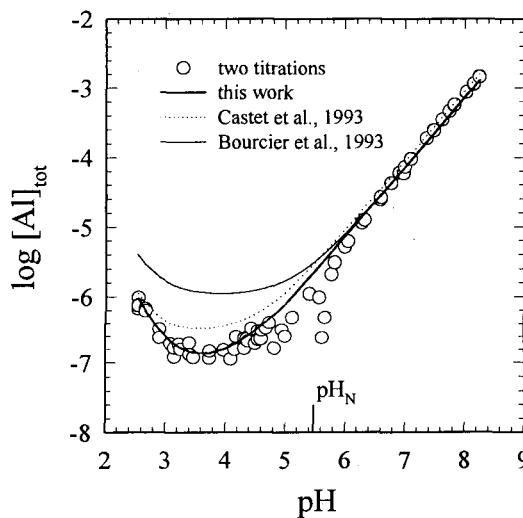


Fig. 2 Solubility profile of boehmite at 203.3°C and $0.03 \text{ mol}\cdot\text{kg}^{-1}$ ionic strength.

It must also be acknowledged that the value for Q_{Ins} used in this fitting process was taken from Castet et al., because, as will be discussed later in the text, the use of the HECC does not extend to low pH values (and high), particularly at low ionic strengths. This is clearly evident from the speciation plot in Fig. 3, which covers the range of pH accessed in the titration, that Al^{3+} is only a minor component of the system at the lowest pH attained and therefore its stability cannot be gleaned from these data alone.

Comparison of the data in Figs. 1 and 2 illustrates the known shift in the position of the solubility minimum to lower pH with increasing temperature, the practical consequence being that the aluminate anion becomes more dominant at high temperatures in natural hydrothermal solutions. Titrations are now in progress at 250°C and a trial experiment is planned for 300°C, which is the working limit of this HECC design.

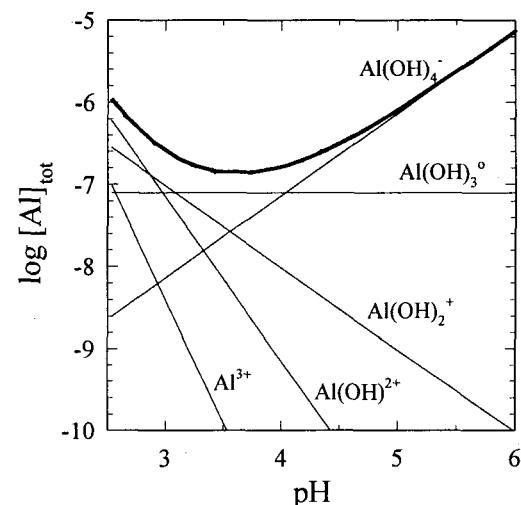


Fig. 3 Speciation diagram for a $0.03 \text{ mol}\cdot\text{kg}^{-1}$ ionic strength solution at 203.3°C saturated with boehmite, where the heavy solid curve represents the total aluminum in solution.

Having shown that the solubility data obtained from potentiometry are compatible with at least one recent study, and emphasizing that these results were obtained in only a fraction of the time required previously, the effect of ionic strength on the solubility of boehmite at high temperatures will now be discussed. There are no preexisting experimental data at these conditions of moderate to high salinity.

High Ionic Strength Results

The solubility of boehmite has been studied at 152.4°C (0.1, 0.3, 1.0 $\text{mol}\cdot\text{kg}^{-1}$), and at 203.3 and 250.0°C (1.0 $\text{mol}\cdot\text{kg}^{-1}$). As processing these combined results requires an overall fit of the individual solubility quotients as functions of temperature and ionic strength, a process that will only be attempted when all of the experimental work is at hand, only the salient features of these results will be presented here. Consider the solubility profile presented in Fig. 4 at 152.4°C and unit ionic strength.

The two values at the beginning of each titration on the acid branch labeled (9 and 5 values) indicate the number of daily samples taken following attainment of thermal equilibrium. The same aluminum content was found within $\pm 2\%$ again attesting to the rapid kinetics of dissolution. The two solid lines are derived from linear regressions with slopes fixed at -3 ($\log Q_{10s}$) and 1 ($\log Q_{14s}$), incorporating in each

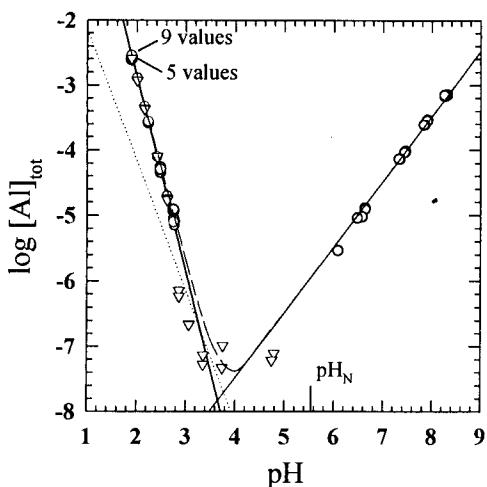


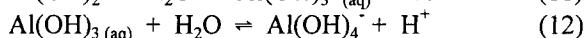
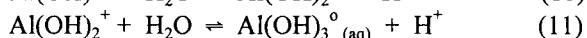
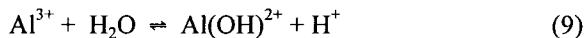
Fig. 4 Solubility profile of boehmite at 152.4°C and 1.0 mol·kg⁻¹ ionic strength. The dotted line stems from Palmer and Wesolowski (1992) for the first hydrolysis quotient.

case the data for $[Al]_{tot} > 10^{-6}$ mol·kg⁻¹. The dotted line was derived for $\log Q_{11s}$ from the first hydrolysis constant of Al^{3+} measured potentiometrically in this laboratory (Palmer and Wesolowski, 1992). The dashed curve represents the total aluminum in solution based only on the three species, Al^{3+} , $Al(OH)^{2+}$, and $Al(OH)_4^-$, establishing that within the accuracy of these experiments, no further species are required to fit the data, with even $Al(OH)^{2+}$ being a minor component over most of the pH range. Indeed, inclusion of Q_{12s} and Q_{13s} values estimated from application of the isocoulombic principle (Lindsay, 1980) for extrapolation of the equilibrium quotients found at 0.03 mol·kg⁻¹ ionic strength, raises the solubility minimum by only 0.4 log units. Considering the analytical difficulties in measuring aluminum concentrations at the minimum of $<10^{-7}$ mol·kg⁻¹, particularly in the presence of high brine concentrations, it would seem adequate for most purposes to either ignore $Al(OH)_2^+$ and $Al(OH)_3^{(aq)}$, or to rely on a method such as the isocoulombic approach to estimate their stabilities at high ionic strength. The destabilization of these hydrolyzed species results from the increased stability of Al^{3+} with increasing ionic strength, which by raising the solubility of boehmite in acidic solution tends to shift acid branch of the solubility profile to higher pH. These comments apply equally to the present results at the other conditions mentioned above, and the same conclusions were drawn from the low

temperature solubility data for gibbsite (Wesolowski and Palmer, 1994).

Hydrolysis Equilibria at Infinite Dilution

The hydrolysis equilibria for aluminum involving monomeric species can be obtained by step-wise algebraic combination of eqns. (2)-(6):



represented by the step-wise hydrolysis constants, K_{01} , K_{12} , K_{23} and K_{34} , respectively. As indicated above there is generally good agreement with the various studies of the first hydrolysis constant, K_{01} ($= K_{10s}/K_{11s}$), involving the simple linear relationship between $\log K_{11}$ and the reciprocal temperature in Kelvin to 200°C proposed earlier by Wesolowski and Palmer (1994) and shown in Fig. 5.

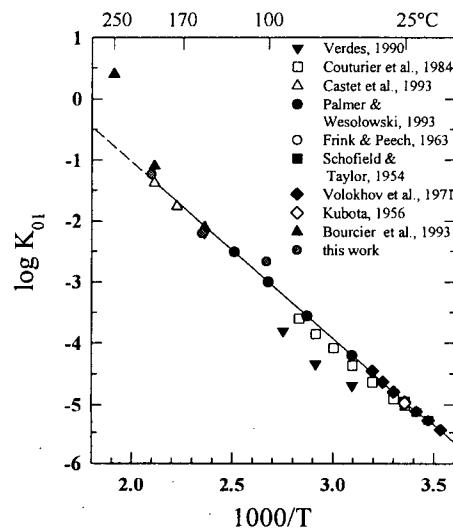
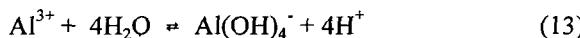


Fig. 5 First hydrolysis constant (eqn. 9) of Al^{3+} (refs. in Wesolowski and Palmer, 1994)

It can be clearly seen that the present results are in reasonable agreement with this established correlation, with the exception of the value at 100°C which requires further investigation. Indeed single batch-type experiments are in progress at higher acid concentration than could be achieved by the current potentiometric method (remembering that the cell configuration requires that $m_3 < m_4$, where m_4 approximately equals the ionic strength). Space does not permit the other hydrolysis figures to be shown,

but as indicated by Wesolowski and Palmer (1994) the $\log K_{n,n+1}$ versus $1/T$ relation becomes less well defined with increasing degree of hydrolysis. The impact of these new data will not be felt until the entire temperature profile is researched, particularly with regard to the solubility minimum where the preliminary results indicate significantly lower stabilities of the neutral $\text{Al(OH)}_3^{(aq)}$ species with increasing temperature.

Certainly, the stabilities of the end-members of the hydrolysis series, Al^{3+} and Al(OH)_4^- , are well defined, so that if the overall equilibrium is written:



then the agreement between the various studies is sound, with the exception of only one study (Verdes, 1990). In view of the overall dominance of the aluminate ion at high temperatures in basic to neutral pH solutions, it is important (and not fortuitous) that the stability of this ion is the most well established.

CONCLUSIONS

Methodology

Benefits:

1. The HECC has provided the first *in situ* high-temperature measurement of pH in a solubility experiment where, in the case of aluminum on the acid branch, the solubility of the solid phase depends to the third power on the hydrogen ion concentration. Thus no pH buffering agents are required that may interact with the solution species or the solid surface. This technology has also been applied successfully to the studies of the solubility of brucite (Brown et al. 1996) and zinc oxide (Palmer and Wesolowski, 1995).
2. The existence of equilibrium conditions can be established from under- or over-saturation by addition of the appropriate titrant.
3. The kinetics of precipitation and dissolution can be monitored efficiently, with or without sampling, using pH as an indicator of reaction progress, either dynamically or in pH-statt mode. Kinetics can be followed isothermally by perturbing the equilibrium condition with addition of an appropriate titrant under conditions either close to equilibrium, or from a high degree of under- or over-saturation.
4. The effects of complexation on the solubility of a given solid phase can be measured yielding

formation quotients for the complexes formed in solution.

5. The prevailing hydrogen gas in the HECC allows control of the hydrogen fugacity within practical limits for solubility studies of a reducing system.
6. It has already been demonstrated in this laboratory that the HECC can be utilized to measure surface adsorption of hydrogen ions on metal oxide surfaces to high temperatures and ionic strengths (Machesky et al., 1994).

Limitations:

7. The system must be inert to reduction by the hydrogen atmosphere present inherently in the HECC.
8. The rate of attainment of equilibrium between the two phases must be rapid enough to make these measurements practical (i.e., on the order of a day or less) to avoid slow contamination of the reference solution, although measures can be taken to refurbish this solution *in situ*.
9. The use of Teflon within the cell imposes an upper practical working limit of 300°C.
10. The dissolved species should not be volatile at high temperature due to the commonality of the vapor space connecting the test and reference solutions.

Aqueous Aluminum Chemistry

These conclusions are general and were not necessarily derived originally from this investigation.

1. Only one solid phase, namely boehmite, was present over the ranges of pH (2-10) and temperature (100-250°C) studied to date.
2. Hydrolysis increases with increasing temperature, such that the solubility minimum moves to lower pH and decreases in depth slightly. Thus in most hydrothermal systems the Al^{3+} ion is not a significant species.
3. The effect of increasing ionic strength is to shift the solubility minimum to higher pH and minimize the stability fields of the hydrolyzed species other than the tetrahedral aluminate anion.
4. The stability fields of the intermediate hydrolyzed aluminum species are narrow with respect to pH at moderate to high ionic strengths. However, their stabilities can be estimated adequately from low ionic strength data using the isocoulombic treatment. Thus, fewer experiments are in order to fully characterize the thermodynamics of the aqueous aluminum system.

5. In the HECC the kinetics of approach to equilibrium were orders of magnitude faster than reported for conventional batch experiments at comparable conditions, although at near neutral pH insufficient time may have been allowed to attain equilibrium aluminum concentrations when approached from under-saturation. Otherwise the equilibria were readily reversible.
6. The equilibrium solubility profiles could be explained completely by the existence of mononuclear aluminum species in solution.

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