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SOLUBILITY AND REACTION RATES OF ALUMINUM SOLID PHASES UNDER GEOTHERMAL CONDITIONS

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ABSTRACT

Experimental studies involving equilibrium solubility and dissolution/precipitation rates were initiated on aluminum hydroxide phases prevalent under geothermal reservoir conditions. A large capacity, hydrogen-electrode concentration cell (HECC) was constructed specifically for this purpose. This cell provides continuous, accurate *in situ* pH measurements of solid/solution mixtures to 295°C with provision for either removing solution samples for analysis of the metal content, or adding either of two titrants. The cell was first used to measure the solubility of pure synthetic boehmite (AlOOH) in NaCl brines over a wide range of pH (2-10), temperature (100 to 290°C), and ionic strength (0.03-5 molal NaCl). This represents the first such study ever reported of mineral solubility profiles across the entire pH range of natural waters at temperature above 100°C, including direct pH monitoring. A least-squares regression of the results obtained at 0.03 ionic strength was used to determine the molal solubility products (Q_{s0} to Q_{s4}) of boehmite, which allows comparison with those constants obtained from two recent high-temperature studies of boehmite solubility that relied on the conventional batch technique.

The ability to perturb pH isothermally by addition of acidic or basic titrant opens the door for studies of the kinetics of dissolution/precipitation, even for relatively fast reactions. Therefore studies of the dissolution/precipitation rates of boehmite (from 100 to 290°C) and gibbsite (50°C) were initiated in neutral to basic solutions at 0.1 molal ionic strength. The results of these experiments and their significance in natural and industrial systems will be discussed.

We have extended this work to include studies of gibbsite at different temperatures (30-70°C), ionic strengths (0.03-1 molal NaCl) and pH's (acidic and basic media), as well as the study of kaolinite and more complex aluminosilicate phases.

1. INTRODUCTION

Aluminum is a major component of most geothermal reservoir rocks. Aluminosilicate transformations and dissolution/precipitation reactions often influence porosity and permeability changes in reservoirs, recharge zones, reinjection sites, and scale formation in production wells. However, despite extensive studies of aluminum in the last decades, large disparities still exist in our ability to predict the dissolution, transport, and precipitation of aluminum in natural systems. The measured (e.g., Bourcier et al., 1993; Castet, et al., 1993; Wesolowski and Palmer, 1994; Anderson, 1995; White and Brantley, 1995, Bénézeth et al., 1997) or estimated (e.g., Pokrovskii and Helgeson, 1995, or predictions from the SUPCRT92, Chiller, and EQ3/6 programs) solubilities and speciation differ by orders of magnitude, especially when compared to actual field observations where near-neutral solutions abound, close to the minimum in the solubility of these aluminum phases. Also, solution equilibria and solubilities must be accurately known in order to interpret kinetic studies of mineral dissolution and precipitation. Dissolution rates of aluminum oxide and hydroxide as a function of temperature, acidity, ionic strength, and degree of saturation have been addressed in previous work (see for example White and Brantley, 1995) and will not be reviewed here. Major aims of previous gibbsite studies were to address the effect of acid rain on aluminum mobility and toxicity (in acidic conditions), as well as at extreme acidic and basic conditions for the aluminum industry (Bayer process). To our knowledge, no rate measurements of boehmite have been reported in the literature.

In this study, boehmite and gibbsite (previously studied in this laboratory, see Palmer and Wesolowski, 1992; Wesolowski, 1992; Wesolowski and Palmer, 1994) were chosen in order primarily to: 1) determine the thermodynamics of aqueous aluminum species; 2) incorporate the data obtained into chemical reaction and transport computer codes; and 3) study their dissolution/precipitation rates. This work is a precursor to unraveling the solubility behavior and reaction rates of more complex aluminosilicate minerals prevalent in geothermal reservoirs.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1 Stock solutions

All solutions were prepared from reagent grade chemicals and distilled deionized water (resistivity 0.18 MΩ-m). Concentrated stock solutions of NaCl, NaOH, and HCl were used to make up the desired experimental solutions.

2.2. Synthesis and characterization of aluminum solid phases

The method of boehmite synthesis and characterization has already been published (e.g., Castet, et al., 1993, Bénézeth et al., 1997). The gibbsite used in this study is from Alcoa (C33), pretreated following the procedure of Bloom and Weaver (1982) and Wesolowski (1992). X-ray diffraction (XRD) and surface area analyses of the starting gibbsite material show that it is well crystallized with a very low surface area of 0.29 m^2/g measured by 5-point N_2 adsorption isotherms (BET), in agreement with the various values reported in the literature. Scanning Electron Microscopy images of the starting material shows that the grains are aggregates of tabular and prismatic crystals typical of a synthetic gibbsite. In all cases, XRD, SEM, and BET were used to confirm the crystallinity and surface area of boehmite and gibbsite samples taken before and after a number of solubility and kinetic experiments.

2.3. Experimental procedure

The HECC has been described in numerous publications (e.g., Bénézeth et al., 1997, 1999) and was used in this work for the solubility measurements and to study the kinetics of dissolution/precipitation of aluminum solid phases. The initial configuration of the cell in a typical experiment containing identical acidic solutions is as follows:

$$H_2\,,Pt\;|\;HCl, NaCl\;||\;HCl, NaCl, S\;|\;Pt, H_2$$

Reference Test

where S represents an aluminum solid phase. After equilibration at temperature, each electrode responds exactly Nernstian to the half cell reaction, $H_{2,g}\ \Omega\ 2H^+ + 2e^-$. Since the cells share a common hydrogen fugacity, the potential between the electrodes is defined as:

$$\Delta E = -(RT/F)\ln(aH^+_{test}/aH^+_{ref}) + E_{lj} \qquad (1)$$

A solution of known pH_m is used in the reference cup and an identical large excess of inert salt is added to both cups, such that the activity coefficient differences and liquid junction potentials (E_{lj}) between the solutions are minimized. Consequently, the pH_m of the test solution can be very accurately determined (to 0.001 pH_m units) and also monitored continuously over time frames of seconds in kinetic titrations, up to months in long-term solubility experiments. Note that the working definition of pH_m throughout this study is $pH_m = -\log[H^+]$ in molal concentration units. The convention used in our laboratory is that H^+ is not complexed by the medium ions and any ion pairing is treated implicitly by the activity coefficient model employed. The pH_m can be readily converted to the activity scale by applying an appropriate activity coefficient/ion pairing model.

In most of the solubility experiments, acidic solutions are first allowed to equilibrate with the solid. Aliquots of the test solution are then withdrawn through a platinum dip tube gold-welded to a platinum frit to prohibit particles entering the platinum tube that may cause precipitation during the sampling process. The platinum sample line is fitted with a cooling jacket and samples are withdrawn for chemical analysis via a PEEK® valve and a 0.2 µm fluoropolymer filter into preweighed polypropylene syringes containing a known mass of high purity 1M HCl.

When equilibrium has been reached, a small amount of NaOH + NaCl, at the same ionic strength as the reference and test solutions, is titrated into the cell from a calibrated positive displacement pump. Generally, the pH_m stabilizes at the new equilibrium value within *ca.* 8 hours (at temperature >100°C) and another sample can be taken for total aluminum analysis. This stepwise process can be repeated to vary pH_m so that the entire solubility profile can be mapped out, or to initiate and follow changes in pH_m as a function of time to extract the kinetics of either the dissolution or precipitation process. A second inert positive displacement pump containing HCl + NaCl at matching ionic strength is available so that the titration process can be reversed (super-saturation to undersaturation and vice versa), or initiated in the case where the experiment began on the basic side.

Analyses of aluminum content are performed by Ion Chromatography (see Wesolowski and Palmer, 1994) or by a colorimetric method, using pyrocatechol violet as chromogenic reagent (Dougan and Wilson, 1974), depending on the aluminum concentration.

3. RESULTS AND DISCUSSION

3.1 Boehmite solubility

Each isothermal set of resulting “pH profiles” (e.g., Fig. 1), which in some cases comprised up to five individual experiments, was treated to yield the solubility quotients, Q_{sn} (n=0-4), corresponding to the reaction:

$$AlOOH_{(s)} + (3-n)H^+\ \Omega\ Al(OH)_n^{3-n} + (2-n)H_2O \qquad (2)$$

The quotients for the end-member species (i.e., Al^{3+} and $Al(OH)_4^-$) and selected values at infinite dilution from the literature, have each been fitted as functions of temperature and ionic strength, including the appropriate Debye-Hückel terms.

As an example, Figs. 2a and 2b represent the logarithm of the respective solubility quotients for the reactions:

$$AlOOH_{(s)} + 3H^+\ \Omega\ Al^{3+} + 2H_2O \qquad (3)$$

$$AlOOH_{(s)} + 2H_2O\ \Omega\ Al(OH)_4^- + H^+ \qquad (4),$$

The solubility constants obtained from the fit at infinite dilution are in good agreement with the studies of Verdes et al. (1992), Castet et al. (1993) and Bourcier et al. (1993) in acidic and basic branches, as can be seen in Figs. 2a and 2b, respectively. However, lower solubilities were obtained at the minimum of the solubility with increasing temperature compared to these authors and the predictions of Pokrovskii and Helgeson (1995). In our experiments equilibrium was approached from supersaturation at the solubility minimum and consequently the measured lower solubilities cannot be due to insufficient equilibration times. These differences likely stem from the use of direct pH measurements, which do not necessitate the use of pH buffers and/or mass balance equations to determine the pH at high temperatures, as were required in the previous batch investigations.

The observed effect of increasing ionic strength (from 0.03 to 5 molal) is a shift in the solubility minimum to higher pH_m, increasing the stability field of Al^{3+} and minimizing the stability fields of the hydrolyzed species other than the aluminate anion. For example, in acidic solutions an increase in salinity from 0.03 to 1 molal increases boehmite solubility by 1.2 orders of magnitude. It appears likely that such conditions can be achieved either in soil and surface waters affected by acid rain and acid mine drainage, or by condensation of acid-volatile-rich steam in geothermal systems, or in hydrothermal ore deposits, etc.

Note that two manuscripts describing the thermodynamics of beohmite dissolution were submitted to Geochim. Cosmochim. Acta (Palmer et al., 2000a; Bénézeth et al., 2000) and one is currently in preparation (Palmer et al., 2000b).

3.2. Dissolution/precipitation rates

The rates of boehmite and gibbsite dissolution/precipitation have now been investigated in basic media. These reactions are less complicated to study compared to the acid analogues in that, over wide pH, temperature and salinity ranges, relevant to conditions found in various geothermal and industrial systems, aluminate is the dominant species.

Boehmite dissolution /precipitation rates

A boehmite kinetic experiment was initiated at 100.3°C and 0.1 molal NaCl ionic strength, whereby 2.57g of boehmite (surface area of $1.95m^2/g$) were suspended in 300g of 0.002 molal NaOH, 0.098 molal NaCl. Following the addition of acidic titrant (0.03 molal HCl, 0.084 molal NaCl), the cell potential, temperature and pressure were recorded as a function of time. Finally a sample of the solution was withdrawn after 24 hours for analysis of aluminum by spectrophotometry. In this case equilibrium was approached from supersaturation with respect to boehmite, thereby allowing us to follow the kinetics of the precipitation reaction. Several subsequent precipitation steps were performed involving sampling the solution after each step. As the near-neutral pH region was approached, several additions of a basic titrant (0.03 molal NaOH, 0.071 molal NaCl) were then made so that the kinetics of the dissolution reaction could be followed. The temperature was then raised to 152.4°C to begin a new set of precipitation/dissolution reactions and so on up to 290.1°C.

The rates of boehmite dissolution and precipitation according to the following reactions:

$$Al(OH)_4^- + H^+ \leftarrow AlOOH_{(s)} + H_2O \qquad k_{diss} \qquad (5)$$

$$Al(OH)_4^- + H^+ \rightarrow AlOOH_{(s)} + H_2O \qquad k_{prec} \qquad (6)$$

are relatively fast at high temperature, so that only the dissolution runs performed at 100.3°C could be analyzed in detail. However, the equilibrium solubilities obtained after each addition of acid or base (see arrows in Fig. 1 as an example at 152.4°C) are in excellent agreement with our previous solubility measurements (solid lines in Figs. 1 and 3) performed at the same conditions (from 100.3 to 290.1°C, 0.1 NaCl) as can be seen in Fig. 3.

The recorded pH_m readings at 100.3°C from the two boehmite dissolution experiments were converted to total aluminum molality $[Al(OH)_4^-]$ based on the known stoichiometry of reaction (5) and the measured aluminum concentration at the end of each step. Both plots followed an exponential dependence with time as equilibrium was approached. “The principle of detailed balancing” (see, Rimstid and Barnes, 1980; Lasaga 1998) was applied under the assumption that the dissolution rate obeys a zero-order dependence (based on Eq. 5):

$$d[Al(OH)_4^-]/dt = k_{diss}C \qquad (7)$$

where C stands for the ratio of total surface area of boehmite to the mass of solution. Similarly, based on equation (6), the precipitation rate of boehmite must obey a second-order rate law:

$$-d[Al(OH)_4^-]/dt = k_{prec}\, C\, m_{H+}m_{Al(OH)4-} \qquad (8)$$

Combining Eqs. (7) and (8) at equilibrium gives:

$$d[Al(OH)_4^-]/dt = k_{diss}\, C - k_{prec}\, C\, m_{H+}m_{Al(OH)4-} = 0 \quad (9)$$

Thus a plot of rate, $d[Al(OH)_4^-]/dt$, versus $m_{H+}\cdot m_{Al(OH)4-}$ is linear, as shown in Fig. 4, with an intercept and slope proportional to the respective rate constants. The ratio of the forward and reverse rate constants must then be equal to the overall equilibrium solubility quotient, Q_{s4}. For the two dissolution steps investigated, the values of $\log(k_{diss}/k_{prec})$ are in excellent agreement, within 0.1 log units, of the corresponding equilibrium constant obtained from the fit shown in Fig. 2b at the same conditions (100.3°C, 0.1 molal NaCl, $\log Q_{s4}$,=-12.74).

Boehmite proved to be an ideal phase, in that its dissolution/precipitation kinetics permitted demonstration of reversible equilibrium solubilities at all temperatures studied and no other phases formed as a result of incongruent dissolution or precipitation from a supersaturated state.

Gibbsite precipitation rates

Similar experiments were initiated with gibbsite at 50.1°C and 0.1 molal NaCl ionic strength, whereby 1.91g of gibbsite were suspended in 90 g of 0.002 molal NaOH, 0.098 molal NaCl. The equilibrium solubilities (Q_{s4}) performed at 50.1°C in the HECC for the following equation:

$$Al(OH)_{3(s)} + H_2O\ \Omega\ Al(OH)_4^- + H^+ \qquad (10)$$

proved to be in excellent agreement with the previous gibbsite solubility obtained at the same conditions using the batch method by Wesolowski (1992) over the pH range (from 10.3 to 8.4).

The first precipitation runs (two single experiments with same solid/solution ratio) also showed a smooth exponential approach to equilibrium as reflected in the $m_{Al(OH)4}^-$ versus time plots in Fig. 5.

Assuming the same reaction mechanism as developed for boehmite, the values of $\log(k_{diss}/k_{prec})$ are also in excellent agreement with our previous solubility data of Wesolowski (1992) ($\log Q_{s4}$,=-13.86) within 0.1 log units.

As these kinetic experiments are still in progress no further details can be given at this time in terms of confirmation of the proposed rate law. However, the results obtained thus-far establish that the dissolution/precipitation rates of both boehmite and gibbsite can be studied accurately and expediently using the unique capabilities of the HECC. By monitoring the change in pH with time, valuable kinetic information can be obtained without the need for sampling. In fact, as the principle of detailed balancing works for boehmite and gibbsite, we anticipate that their dissolution and precipitation rates can be obtained in this manner. Nevertheless, this hypothesis will be checked experimentally. In addition to reaction variables such as pH_m, temperature, pressure, and surface properties, several other experimental variables will be evaluated, namely, stirring rate, solid/solution ratio, and salinity.

4.CONCLUSION

A completely consistent set of thermodynamic parameters generated in this study define the prevalent aqueous aluminum species, as well as the chemical composition of solutions in equilibrium with rock-forming minerals from ambient to geothermal reservoir conditions. These results are being treated to allow them to be readily incorporated into chemical reaction and transport computer codes in common use by the geothermal industry such as Chiller or EQ3/6.

Finally, we will investigate aluminosilicate solubility equilibria and kinetics by first determining the dissolution and precipitation kinetics of increasingly complex aluminosilicates, such as kaolinite, dickite and feldspars bearing in mind applied problems associated with brine reinjection, scaling, and corrosion in down-hole and in-plant systems.

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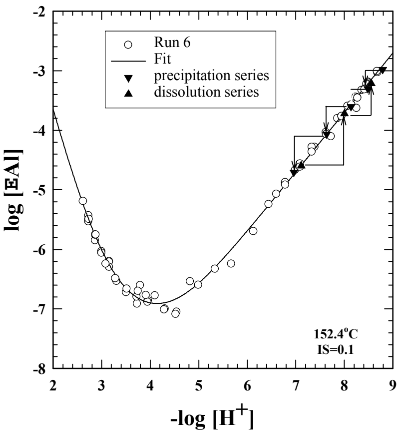

Figure 1: Solubility and dissolution/precipitation kinetics of boehmite at 152.4°C and 0.1 molal NaCl

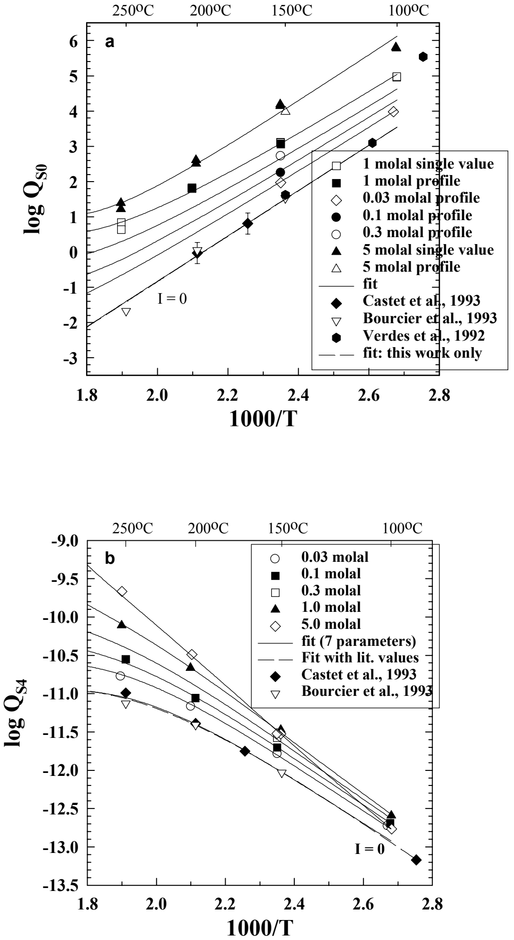

Figure 2: Boehmite dissociation quotients, $\log Q_{s0}$ (a) and $\log Q_{s4}$ (b) as a function of the reciprocal of temperature. Comparison with literature data at infinite dilution.

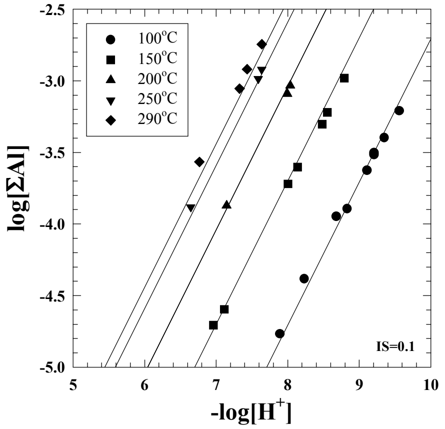

Figure 3: Solubility of boehmite (steady state) from precipitation/dissolution kinetic at 0.1 molal ionic strength and as a function of pH and temperature. The solid lines represent the solubility obtained from the fits reported in Fig. 2b.

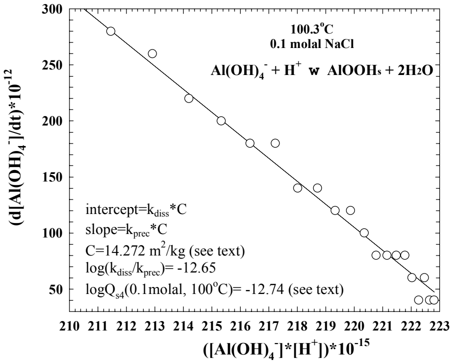

Figure 4: Boehmite dissolution rate at 100.3°C, 0.1 molal ionic strength.

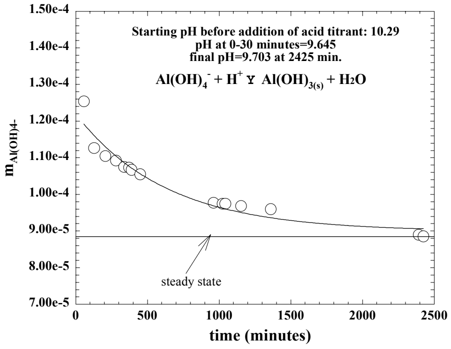

Figure 5: Gibbsite precipitation step at 50.1°C, 0.1 molal ionic strength.