Organization	Oak Ridge National Laboratory

Project Title:

As yet unpublished, isopiestic data on sodium aluminate solutions from 110 to 169°C are available from the work of Howard Holmes (retired) carried out in our laboratory for the geothermal program.
Due to the restricted concentrations of aluminate that could be reached in these solutions, modeling of the resulting osmotic/activity coefficients according to the Pitzer ion-interaction model proved to be ambiguous. The cause of this problem rests with the pure $NaAl(OH)_4$ parameters, which could not be uniquely specified without having data at high mole fractions of this salt. Although solubility data exist in the literature for boehmite in relatively high caustic solutions, it was decided to conduct some batch experiments to verify the accuracy of these results and to provide the needed high aluminate concentrations that would contribute to the modeling effort. A series of experiments was conducted from 100 to 200°C in a Teflon-lined autoclave up to approximately four molal total NaOH, with aluminate concentrations up to 1.9 molal. Beyond this concentration, precipitation of an aluminate phase occurred in the sampling lines dictating the upper concentration limit for these experiments. A preliminary Pitzer model of the $NaAl(OH)_4$ - NaOH system using these results and selected studies taken from the literature is complete. This model is not only consistent with our previously published, low temperature (<80°C) results based on gibbsite solubility experiments, but only required three independent variables (temperature-dependent terms) to fit the ion interaction parameters for the entire system. Two manuscripts describing the thermodynamics of boehmite dissolution are currently in preparation.

By monitoring the change in pH with time, considerable kinetic information can be obtained without the need for sampling. Therefore, studies of the dissolution/precipitation rates of boehmite were initiated in neutral to basic solutions at 100 to 290°C at 0.1 molal ionic strength. In FY 2000, the dissolution/precipitation kinetics and solubilities of aluminosilicates will be studied with the intent of addressing problems associated with brine reinjection, scaling, and corrosion in down-hole and in-plant systems. Studies will involve equilibrium solubility and dissolution/precipitation rate determinations of gibbsite at low temperature (50-70°C), and for a number of aluminosilicate phases prevalent in geothermal reservoirs at higher temperatures, using the hydrogen-electrode concentration cell. The principal limiting factor in the use of these cells will be the formation of additional phases during the course of the experiments. Therefore, we will first initiate studies of gibbsite, for which equilibrium data are available from earlier work in this program and we know that at least in the case of the dissolution reaction, no other phases are formed. We will then undertake to investigate aluminosilicate solubility equilibria and kinetics by first determining the dissolution and precipitation kinetics of increasingly complex aluminosilicates, such as kaolinite, dickite and feldspars. Natural kaolinite from Decazeville, France, is already available and will be used after treatment to remove traces of iron oxide.

The hydrogen-electrode concentration cell approach is also entirely amenable to studies of the rates and equilibrium constants of mineral transformation reactions, such as the hydrolysis of feldspars via reactions such as the alteration of potassium feldspar to muscovite and quartz:

$$3KAlSi_3O_8 + 2H^+ \rightleftharpoons KAl_3Si_3O_{10}(OH)_2 + 2K^+ + 6SiO_2$$

If these phases react sufficiently rapidly to achieve equilibrium in a few weeks at temperatures of 200-300°C in our cells, which are magnetically stirred with high efficiency promoting rapid attainment of solid/liquid equilibrium, the kinetics will be investigated in detail. This knowledge will aid in predicting pH, steam corrosivity and scale formation in geothermal systems. Furthermore, by first establishing an equilibrium K^+/H^+ ratio, then quickly changing this ratio by titration of acid, base, or potassium into a solution in equilibrium with the mineral assemblage, and monitoring pH to a new equilibrium value, we can obtain the rates of reaction, both at near- and far-from-equilibrium conditions, as a function of temperature, pH, salinity, and mineral grain size. This will enable us to test commonly used fluid geothermometers, determine the pH imposed by various mineral assemblages on circulating brines, and help lay the framework for realistic fluid/rock interaction rate models.

FY 1998 and 99 Results: During FY 1998 and 1999, the final experiments were performed to complete the study of the solubility of boehmite from 100 to 290°C in brines at concentrations from 0.03 to 5 molal. These final experiments involved four sets of solutions at 1 and 5 molal (NaCl). For two sets the batch sampling mode was used as the pH was controlled with excess HCl, so that the dominant aluminum species in solution was Al^{3+}. The remaining experiments were performed in dilute NaOH where the aluminate anion predominates and it was therefore necessary to measure the pH *in situ* with the ORNL's unique hydrogen-electrode concentration cell. The previous boehmite work focused on measuring the pH dependence of the solubility isothermally, mainly at lower ionic strengths. Each isothermal set of resulting "pH profiles", which in some cases comprised up to five individual experiments, has now been treated to yield the solubility quotients, Q_{sn} (n=0-4), corresponding to the reaction: $AlOOH_{(s)} + (3-n)H^+ \rightleftarrows Al(OH)_n^{3-n} + (2-n)H_2O$. These quotients, together with those alluded to above for the end-member species and selected values from the literature, have each been fitted as functions of temperature and ionic strength, including the appropriate Debye-Hückel terms. Two manuscripts describing these results and the experimental approach are being prepared. Moreover, these functions have been used to generate new parameters for the Chiller and EQ3/6 commercial programs and these are now being tested against our most recent data.

As an example, Figure 1 represents the logarithm of the solubility quotients for the reactions:

$$AlOOH + 3H^+ \rightleftarrows Al^{3+} + 2H_2O \qquad Q_{s0}$$
$$AlOOH + 2H_2O \rightleftarrows Al(OH)_4^- + H^+ \qquad Q_{s4}$$

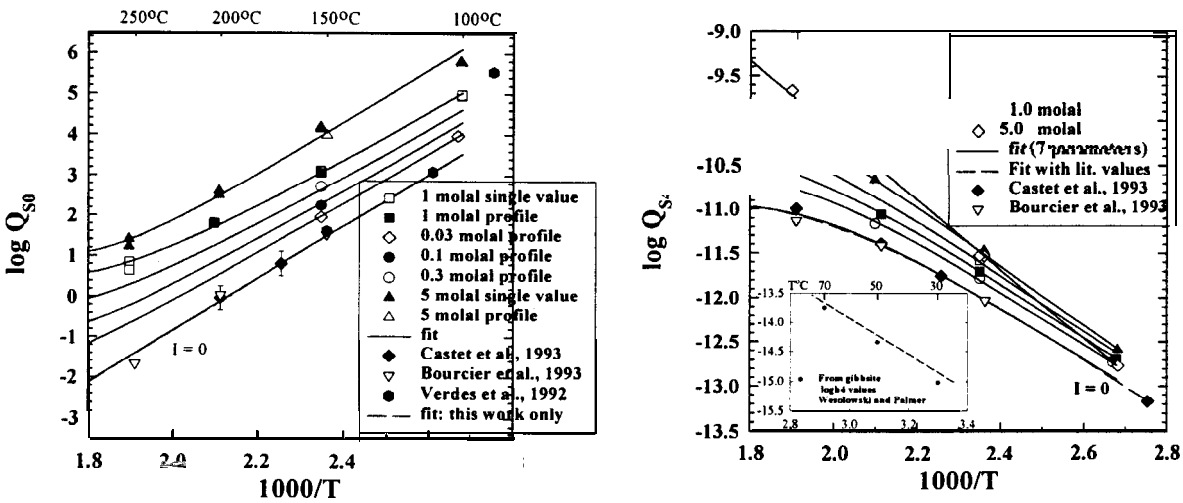

Figure 1

obtained in the present study as a function of reciprocal of temperature, at different ionic strengths, and compared with the literature values at infinite dilution.

Note that one solubility experiment was performed involving gibbsite in contact with an acidic saline solution (I=0.03

method (Palmer and Wesolowski, 1992) using a different source of purified gibbsite. This is not only very reassuring in terms of the intrinsic reliability of the results obtained in this research program, but also opens the door for future kinetic studies on gibbsite with this unique technique.

A logical extension of the solubility studies on boehmite in NaCl brines was to conduct a number of solubility studies in tetramethylammonium chloride (TMACl) solutions in moderately basic solutions at 200°C (I = 0.1 molal). The large, singly-charged TMA' cation is known to form very weak ion pairs with singly-charged aqueous anions. We therefore attempted to use this approach to determine the extent of ion pairing between the aluminate anion $Al(OH)_4^-$ and Na', by titration of a NaCl/NaOH solution into the hydrogen-electrode concentration cell. Recent literature studies provide conflicting ion pair association constants for this interaction. However, we were unable to detect any increase in solubility with increasing sodium concentration and can therefore only place a possible maximum value on this constant at this time. We have successfully completed the first stage of the modeling program for the $NaAl(OH)_4 - NaOH$ system. The modeling effort is based on the Pitzer ion interaction treatment, incorporating the osmotic coefficient data (1 IO- 169°C) from Howard Holmes (retired, ORNL) and equilibrium solubility quotients for the reaction:

$$AlOOH + OH^- + H_2O \rightleftharpoons Al(OH)_4$$

These quotients were either obtained in the current geothermal program late last year (a limited number of experiments at 100, 150 and 200°C), or found in the literature as summarized by Apps, Neil and Jun,

is re
ell et al. (1955),
pure
ger
ssoci
son (
con
ng parameters $\theta_{OH,Al(OH)4}$ and $\psi_{Na,OH,Al(OH)4}$,
based on the equivalent gibbsite solubility
our boehmite solubility data. It was found
fit the entire boehmite so
rature-dependent terms were in the parame
points were then excluded from the fit, in
btain the optimum fit factor.

ınd
analyzed

Technology Integration: A consistent set of thermodynamic parameters generated in this program define the prevalent aqueous aluminum species, as well as the chemical composition of solutions in equilibrium with rock-forming minerals, at geothermal reservoir conditions. The 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. We have been in contact with Dr. Mark Reed (Department of Geological Sciences, University of Oregon) who has provided us with a number of databases (Soltherm) for the program Chiller, which we have tested against our most recent results. Moreover, we have had contact with Dr. Thomas Wolery (LLNL) concerning the EQ3-6 database (data0) and are currently making modifications to it in order that it be consistent with our experimental results. We had direct contact with Dr. Darrel Gallup (Unocal Corp.) concerning problems associated with collection and storage of field samples for aluminum analysis. In general, the dissolution/precipitation kinetics and solubilities of aluminosilicates will be studied with the intent of addressing problems associated with brine reinjection, scaling, and corrosion in down-hole and in-plant systems.

Acknowledgments

This research was sponsored by the Office of Basic Energy Sciences and the Office of Energy Efficiency and Renewable Energy, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

References:

Apps J.A., Neil J.M. and Jun C.H. (1989)Tbermochemical properties of gibbsite, bayerite, boehmite, diaspore, and the aluminate ion between 0 and 350°C. *Div. Waste Mgt., Office of Nucl. Material Safety and Safeguards, US NRC NUREG/CR-5271-LBL 21482.*

Bemshtein V.A. and Matsenok Ye. A. (1961) Rastvorimost bemita v shchelochnom rastvore pri 250 i 350°C, [Solubility of boehmite in alkaline solution at 250 and 300°C]. *Zhurnal Prikladnoi Khimii, 38,* 1935-1938.

Bourcier W. L., Knauss K. G. and Jackson K. J. (1993) Aluminum hydrolysis to 250°C from boehmite solubility measurements. *Geochim. Cosmochim. Acta*, **57**, 747-762.

Castet S., Dandurand J. L., Schott J. and Gout R. (1993) Boehmite solubility and aqueous aluminum speciation in hydrothermal solutions (90-350°C). Experimental study and modeling. *Geochim. Cosmochim. Acta*, **57**, 4869-*4884.*

Diakonov I., Pokrovski G., Schott J., Castet S. and Gout R. (1996) An experimental and computational study of sodium-aluminum complexing in [illegible]

20, 76-86.

Magarshak G.K. (1938) Politermy sistemy Al_2O_3-Na_2O-H_2O pri t=30-200°C, [Polytherms in the Al_2O_3-Na_2O-H_2O system at 30-200°C]. *Legkiye Metally*, *7,* 12- 16.

Palmer D. A. and Wesolowski D. J. (1992) Aluminum speciation and equilibria in aqueous solution: II. The solubility of gibbsite in acidic sodium chloride solutions from *30* to *70°C Geochim. Cosmochim. Acta*, *56,* 1093-l 111.

Pokrovskii V. A. and Helgeson H. C. (1995) Thermodynamic properties of aqueous species and the solubilities of