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THE SOLUBILITY OF AMORPHOUS SILICA IN GEOTHERMAL BRINES

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ABSTRACT

The solubility of amorphous silica in geothermal brines can be predicted to 275°C employing the Setchenow equation,

$$\log s = \log s_0 - \Sigma_i (D_i m_i)$$

where s and s_0 are molal solubilities of silica in geothermal brine and pure water, respectively, D is a proportionality constant for a given salt component and temperature, and m is the molality of a salt component. The most important salt components in geothermal brine are NaCl, KCl and CaCl2. Prior to this study, D values were only available for NaCl, Na2SO4, MgCl2, MgSO4, and NaNO3 (Marshall and Chen, 1982). New silica solubility data has been obtained for KCl and CaCl2 and their corresponding D constants to 275°C. This data yields predicted silica solubilities in hypersaline geothermal brines that agree with experimental values.

INTRODUCTION

The solubility of amorphous silica in various electolyte solutions over the temperature range, 25 to 350°C, was studied in detail several years ago (Chen and Marshall, 1982). Silica solubilities were shown to be depressed by the "salting out" effect of sodium chloride, sodium sulfate, sodium nitrate, magnesium chloride and magnesium sulfate compared to pure water. The solubility behavior of silica was predicted for mixed electrolyte solutions from solubility data in the individual salt solution using an additivity principle of the classic Setchenow equation:

$$\log (s_0/s) = D\,m \qquad (1)$$

where s_0 and s are the molal solubilities of amorphous silica in pure water and in the electrolyte, respectively, D is a constant dependent on the electrolyte and temperature, and m is the molality of the electrolyte. The Setchenow equation for mixed electrolytes, which was shown to be valid (Marshall and Chen, 1982) is expressed as:

$$\log (s_0/s(\text{mixture})) = \Sigma_i (D_i m_i) \qquad (2)$$

where i is the the individual electrolyte present in the mixture.

The electrolyte solutions examined in the solubility studies conducted by Marshall and Chen are useful for predicting silica concentrations in sea water and certain brines. In most geothermal brine systems of interest, however, the more common electrolytes are sodium, potassium and calcium chlorides. This is especially true for the hypersaline brines of the Salton Sea, CA geothermal field. Silicate scale deposition has hindered energy extraction efforts in the field (Gallup, 1989). An understanding of amorphous silica solubility in the brine is required to efficiently operate brine treatment facilities at the field and overcome the scale deposition problems (Featherstone and Powell, 1981; Featherstone, 1984).

The present study was initiated to develop predictive capabilities of the solubility of amorphous silica in near-neutral (pH 5 to 8) geothermal brines consisting primarily of sodium, potassium and calcium chloride salts. Attempts were made throughout the experimental, analytical and computational phases of this work to be consistent with the conventions employed by Marshall and Chen.

EXPERIMENTAL PROCEDURES

In contrast to the method employed by Marshall (1980), in which silica solubilities were determined in rocking bombs, the present studies were conducted in a 1 L Hastelloy C-276 autoclave (Autoclave Engineers). Approximately 7 grams of reagent grade silicic acid, washed according to the procedure detailed in Marshall (1980), was placed into the autoclave together with the appropriate electrolyte solution. The head space in the autoclave was purged for several minutes and pressure tested with pre-purified nitrogen. The mixtures were then heated to the appropriate temperature with stirring (~250 rpm). After equilibration at each temperature for a minimum of 3 hours, a 10 mL sample was withdrawn from a sample port cooled with ice water. The aliquot was immediately filtered (0.45 micron Millipore), fixed with dilute ultrapure nitric acid solution and analyzed for silica by inductively-coupled plasma (ICP) spectroscopy. Reagent grade salts were employed throughout the electrolyte studies.

In all experiments, silica solubilities were measured at temperatures during heating and cooling of the autoclave to provide at least two analyses per temperature setting. The silica concentrations from heating and cooling were averaged (reproducibility, ~2%) for a given temperature (+/-2°C).

RESULTS AND DISCUSSION

To determine the validity of the autoclave experiments, the solubility of amorphous silica in pure water was obtained over the temperature range, 25°C to 275°C. The results of this experiment are provided in Table 1. Included in Table 1, for comparison, are the corresponding data obtained by Chen and Marshall (1982). The solubilities in pure water agree very well between the two methods. This gives us confidence in the autoclave approach to measuring silica solubilities. Another test of our method is comparison of solubility data in electrolyte solutions. Table 2 compares the autoclave results of amorphous silica solubility in 3.18 m sodium chloride solution with predicted solubilities employing data from Marshall and Chen (1982) incorporating the Setchenow equation (1). Again, good agreement between the measured and predicted solubilities is obtained, indicating that the present study is consistent with the earlier work (Marshall and Chen, 1982).

For a given molality of electrolyte, the effect on silica solubility was found to dependent upon the cation in the order Mg(+2), Ca(+2), > Li(+) > Na(+) > (K+) (Marshall and Warakomski, 1980). Table 3 shows the dramatic "salting out" effect of magnesium chloride on the solubility of silica compared to an equivalent salt molality of sodium chloride (5.8m). Included in Table 3 are predicted silica concentrations in the salt solutions again using the Setchenow equation (1) (Marshall and Chen, 1982). Magnesium and calcium ions were shown to depress the solubility of silica to the same degree at 25°C (Marshall and Warakomski, 1980). In later publications by Marshall, only magnesium chloride salt effects were examined. To ensure that calcium chloride, a more common component of geothermal brine, behaves similar to magnesium chloride above 25°C, the solubility of silica was studied from 25 to 275°C at 1.02 molal concentration. Table 4 presents the results of this experiment. Table 4 includes calculated solubilities for MgCl2 using the data from Marshall and Chen, and the Setchenow equation (1). The predicted solubilities for MgCl2 compare favorably with the experimental data for CaCl2 obtained in this study. The proportionality constant, D, for MgCl2 (Marshall and Chen, 1982) at a given temperature is essentially equivalent to the D parameter calculated from the CaCl2 experiment. This result implies that solubility data and D values for magnesium chloride can be substituted in the absence of data for calcium chloride in geothermal brines.

Potassium chloride is an important constituent of

hypersaline geothermal brines. Similar to calcium chloride, the only solubility data available for KCl was obtained at 25°C (Marshall and Warakomski, 1982). Table 5 gives the solubility data for silica and the average D values from 25 to 275°C in solutions of potassium chloride. The solubility of silica in KCl is greater than in NaCl, as expected. The value of the D parameter at 25°C given by Marshall and Chen, 0.028, compares favorably with the D value obtained in this study (0.0302). The solubility of silica is depressed, as anticipated, by increasing the concentration of KCl in solution.

Table 6 provides the D constants for the three prevalent electrolytes in geothermal brine over the temperature range, 25 to 300°C. Values for NaCl are those previously published by Marshall and Chen, MgCl2 constants (also previously published) are substituted for CaCl2, and KCl values are given from the results of this study. The MgCl2 constants are used here and below, in place of the CaCl2 constants obtained in the present study, due to the limited number of CaCl2 experiments and the large number of MgCl2 experiments employed to derive the D values.

To check the accuracy of the D values in Table 6 for the three electrolytes, the expanded Setchenow equation (2) was used to predict the solubility of amorphous silica in a simulated Salton Sea geothermal brine that was tested in the autoclave. Table 7 and the Figure show the brine composition and resultant silica concentrations at various temperatures from the experiment. The predicted silica solubilities from Equation 2 and D constants in Table 6 are included for comparison. Agreement between the experimental and predicted solubilities is very acceptable with an average error of only 4%.

With acceptable D parameters in hand for the three predominant electrolytes in geothermal brine, the predictive capability of the Setchenow equation can be tested by comparing calculated vs actual silica concentrations in Salton Sea geothermal brines. Dissolved silica concentrations for several brines that have been stabilized with respect to scale deposition employing crystallizer-clarifier technology (Featherstone, 1984) are given in Table 8. Included in Table 8 are calculated silica solubilities using various combinations of electolytes and assuming that all chloride is present as a given electrolyte. The electrolyte combination that appears to most accurately predict the actual measured silica concentration in stabilized brine over the temperature range, 104 - 147°C, is Na/K/Ca/Cl (where D values for Mg are substituted for Ca, vide supra).

CONCLUSION

Solubilities of amorphous silica have been measured in various aqueous salt solutions of importance to hypersaline geothermal systems. It has been shown that calcium chloride depresses silica solubility to about the same degree as

magnesium chloride. Solubility measurements in potassium chloride over the range of 25 to 275°C at four different molalities has made it possible to accurately predict silica concentrations in hypersaline geothermal brines, such as those encountered at the Salton Sea, CA field. Silica solubilities are predicted using an expanded form of the Setchenow equation. This new capability to predict silica solubilities accurately can be used to determine saturation concentrations of silica in geothermal energy extraction processes, and to predict conditions conducive to silica scale deposition.

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Table 1. The molal solubility of amorphous silica in pure water at various temperatures.

Temperature, °C	SiO2 Solubility, m This Study	SiO2 Solubility, m (Marshall, 1980)*
0		0.00119
25	0.00233	0.00217
100	0.00624	0.00675
150	0.0103	0.0109
200	0.0161	0.0157
250	0.0217	0.0211
275	0.0238	0.0240
300		0.0270

* $\log s_o = -0.1185 - 1.1260\text{E}03/T + 2.3305\text{E}05/T^2 - 3.6784\text{E}07/T^3$

where T is the absolute temperature

Table 2. The molal solubility of amorphous silica in 3.18m NaCl solution at various temperatures.

Temperature, °C	SiO2 Solubility, m This Study	SiO2 Solubility, m (Marshall and Chen, 1982)*
25	0.00073	0.00123
100	0.00368	0.00429
150	0.00653	0.00746
200	0.0116	0.0115
250	0.0162	0.0163
275	0.0190	0.0188

* Equation 1

Table 3. The molal solubility of amorphous silica in 5.8m NaCl and 5.8m MgCl2 at various temperatures.

Temperature, °C	SiO2 Solubility, m	
	This Study	(Marshall and Chen, 1982)*
5.8m NaCl		
25	0.00080	0.00074
100	0.00337	0.00295
150	0.0562	0.0546
200	0.0885	0.0886
250	0.0135	0.0131
275	0.0206	0.0182
5.8m MgCl2		
25	0.00013	0.000073
100	0.00040	0.00038
150	0.00115	0.00089
200	0.00240	0.00200
250	0.00375	0.00430
275	0.00927	0.00931

* Equation 1

Table 4. The molal solubility of amorphous silica in 1.02m MgCl2 and 1.02m CaCl2 at various temperatures with corresponding D constants.

Temperature, °C	1.02m CaCl2*		1.02m MgCl2**	
	SiO2, m	D	SiO2, m	D
25	0.00138	0.194	0.00120	0.254
100	0.00425	0.203	0.00406	0.216
150	0.00687	0.195	0.00701	0.187
200	0.00962	0.208	0.0107	0.154
250	0.0162	0.117	0.0159	0.119
275	0.0193	0.092	0.0190	0.080

* This Study

** Marshall and Chen, 1982

Table 5. The molal solubility of amorphous silica in aqueous KCl solutions at various temperatures.

Temperature, °C	SiO2 Solubility, m				
	0.51m	1.03m	1.04m	2.13m	3.31m
25	0.00209	0.00203			
100	0.00655	0.00646	0.00643	0.00628	0.00581
150	0.0109	0.0104			
200	0.0156	0.0153			
250	0.0209	0.0210			
275	0.0240	0.0237			

Table 6. Values of the D proportionality constant for calculating activity coefficients of amorphous silica in geothermal brine consisting primarily of NaCl, KCl, and CaCl2 at various temperatures.

Salt	D (based on molality)						
	25°C	100°C	150°C	200°C	250°C	275°C	300°C
NaCl a	0.0803	0.0619	0.0515	0.0427	0.0353	0.0330	0.0295
CaCl2 b	0.254	0.216	0.187	0.154	0.119	0.098	0.0796
KCl c	0.0302	0.0199	0.0120	0.0078	0.0032	0.0015	

a. Marshall and Chen, 1982

b. MgCl2 data in Marshall and Chen, 1982

c. This study

Table 7. The molal solubility of amorphous silica in simulated Salton Sea geothermal brine at various temperatures.*

Temperature, °C	SiO2 Solubility, m	
	This Study	Equation 2 (D values, Table 6)
25	0.00093	0.00099
100	0.00338	0.00359
150	0.00626	0.00639
200	0.00983	0.0101
250	0.0143	0.0149
275	0.0149	0.0155

* Na = 43,000 ppm, K = 10,000 ppm, Ca = 18,300 ppm, Cl = 125,000 ppm
Total Dissolved Solids = 200,000

Table 8. Comparison of actual and predicted molal solubilities of
amorphous silica in Salton Sea geothermal brines.

| | SiO2 Solubility, m | | |
	Brine 1 [a]	Brine 2 [b]	Brine 3 [c]
Experimental Value	0.00276	0.00272	0.00568
Predicted Value - Equation 2			
Na/K/Ca/Cl	0.00272	0.00282	0.00554
Na/Ca/Cl [d]	0.00282	0.00302	0.00560
Na/K/Cl [e]	0.00400	0.00498	0.00763
K/Ca/Cl [f]	0.00426	0.00490	0.00780
all Cl as NaCl	0.00295	0.00332	0.00622
all Cl as KCl	0.00538	0.00626	0.00954
all Cl as CaCl2	0.00032	0.00029	0.00144

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a. Na = 59,800 ppm, K = 13,300 ppm, Ca = 26,200 ppm, Cl = 162,000 ppm,
    Total Dissolved Solids = 272,000 ppm. T = 104*C.

b. Na = 62,100 ppm, K = 17,700 ppm, Ca = 32,200 ppm, Cl = 172,000 ppm,
    Total Dissolved Solids = 298,000 ppm. T = 109*C.

c. Na = 50,700 ppm, K = 11,400 ppm, Ca = 22,800 ppm, Cl = 144,000 ppm,
    Total Dissolved Solids = 237,000 ppm. T = 147*C.

d. Contribution of KCl neglected.

e. Contribution of CaCl2 neglected.

f. Contribution of NaCl neglected.

Figure. Amorphous Silica Solubility in
Salton Sea Geothermal Brine