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CALCITE SOLUBILITY IN SIMULATED GEOTHERMAL BRINES

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DISCLAIMER

SUMMARY

The work described in this report was authorized under Contract DE-AC06-76RLO-1830 for the United States Department of Energy, Division of Geothermal energy. Members of The Corrosion and Metallurgy Section, Materials Sciences Department, Pacific Northwest Laboratory performed the work.

The deposition of scale on geothermal piping surfaces has been recognized as a cause of increased pressure drop and diminished fluid flow. The two most common scales encountered in the geothermal energy field are silica and calcite. Calcite scaling potential is the subject of this report.

The main purpose of this study was to obtain accurate, reliable calcite solubility data in brines similar to natural geothermal brines over the temperature range of most known exploitable geothermal resources. In addition, geothermal fluid equilibrium modeling efforts and data bases can be refined and fine-turned with respect to the commercially important calcite-geothermal fluid stability problem with these data.

The effect of sodium chloride and sodium bicarbonate on the solubility of $CaCO_3$ (calcite) in high temperature solutions was measured over the 100°C to 300°C temperature range. The brines studied contained 0 to 5 wt% NaCl, 0 to 5 mM $NaHCO_3$, and 0.003 to 0.1 M CO_2. The data detailing calcite solubility at various temperatures are presented in tabular, graphical, and regression-equation form for each brine composition tested.

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INTRODUCTION

The deposition of scale on geothermal piping surfaces has been recognized as a cause of increased pressure drop and decreased fluid flow. The two most common scales encountered in the geothermal energy field are silica and calcite. Calcite scaling potential is discussed in this report.

The experimental work described here provides a data base that will allow the calculation of calcite scaling potential when geothermal brines of different chemical composition are mixed. Equally important to geothermal energy extraction is calcite precipitation resulting from CO_2 release during flash boiling of the fluid. This latter topic is not specifically addressed in this report.

Brine mixings may occur during three readily identifiable common situations.

1. Water from two aquifers of different chemical composition can mix in a geothermal supply well.
2. Commercial power plants rely on several different wells to supply hot brine to their heat exchangers or flash separator. Each well contributing to the overall flow may have sufficiently different chemical composition such that precipitation (scaling) occurs when the flows are combined or when brine is combined with fluids of a different pH.
3. Reinjection of spent brine may result in scaling where the spent brine meets ground water.

The data base developed here will be used to improve computer models of calcite scaling potential. Ultimately, a realistic computer model along with accurate chemical analyses of brine compositions can be used to predict scaling behavior and potential.

EXPERIMENTAL

In order to measure calcite solubility under high-temperature conditions, several parameters must be accurately measured and controlled.

1. The composition of the simulated brine before it is exposed to solid calcite must be determined.
2. Sufficient equilibration time must be provided for the exposure of the simulated brine to calcite.
3. The exposure chamber must be maintained at sufficient pressure to ensure that the simulated brine remains totally liquid even at temperatures up to 300°C.
4. The temperature at which equilibration takes place must be accurately known.
5. Methods of sampling the equilibrated brine and accurately determining the calcium content of the sample must be available.

The apparatus shown schematically in Figure 1 and described below was designed to satisfy these criteria. The heart of the system is a straight 25-cm length of Inconel® tubing packed with 5-mm and smaller pieces of Iceland spar (calcite). The test solution (simulated brine) is slowly pumped through the calcite-packed tube against a back-pressure controller set at 1900 to 2000 psi. The heated parts of the system are contained within an oven that was originally part of a gas chromatograph (GC). Oven temperature and air circulation are controlled by the original gas chromatograph controls and sensors. The tubing and the fittings in the heated part of the system are either Inconel 600 or Hastelloy C.® Calibrated thermocouples at both the inlet and outlet of the calcite packed tube are directly in the flowing test solution stream. The calcite-packed tube is situated vertically in the GC oven with the solution outlet at the top.

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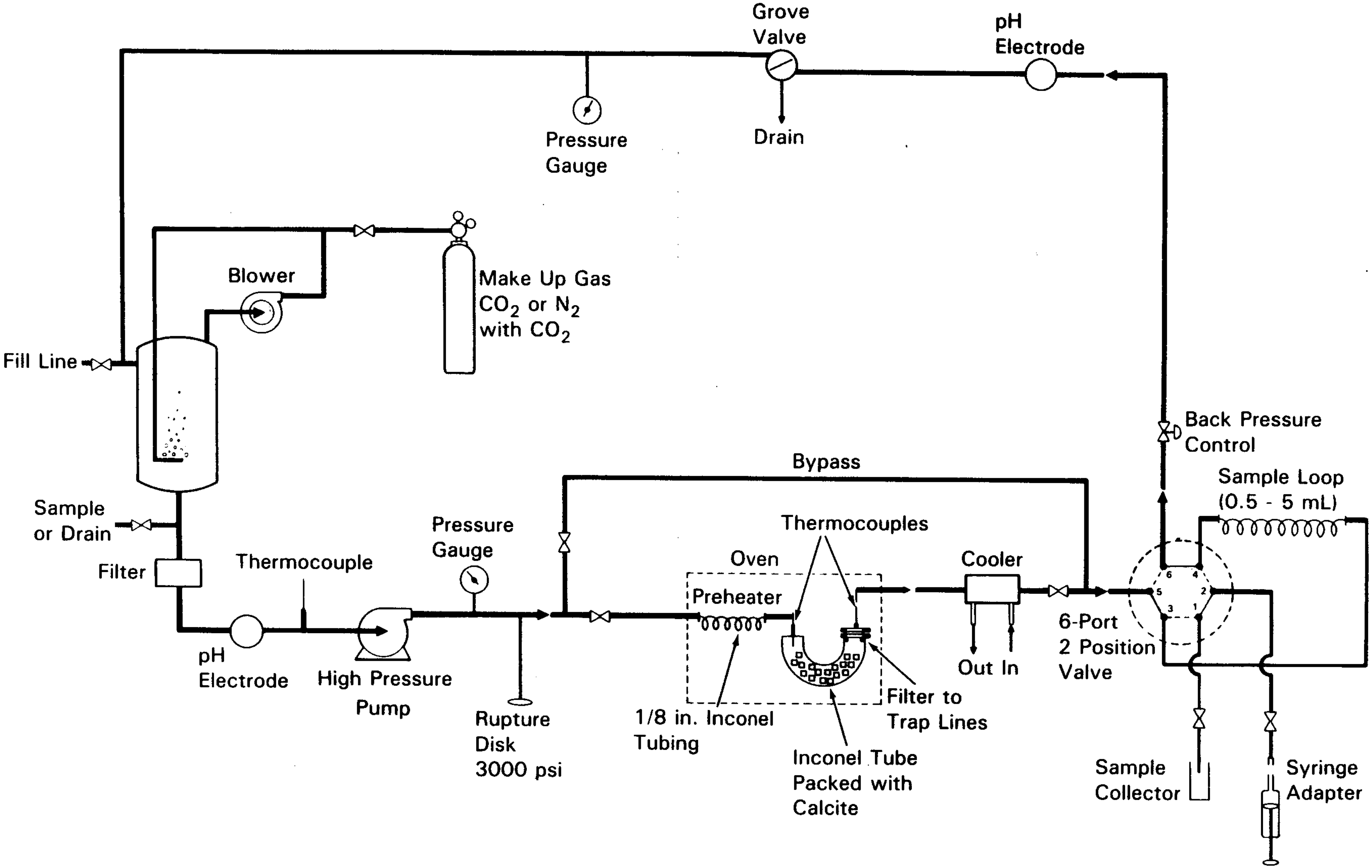

FIGURE 1. Schematic Diagram of Experimental Apparatus

A temperature differential of approximately 5°C on the calcite-packed tube was observed throughout the tests; the higher temperatures were always observed at the solution outlet (top). Therefore, the hottest part of the system, where solution is in contact (and equilibrated) with calcite, is at the end of the contact zone. This situation is preferred in working with a compound like $CaCO_3$, which has a negative temperature coefficient of solubility. The reduced solubility at the higher outlet temperature helps to assure saturation at the outlet. Temperatures given in the data tables, figures, and regression equations throughout the report are those measured at the equilibration column outlet.

A third thermocouple is used to monitor the temperature of the feed solution. The combination pH electrodes are used to monitor the chemical stability of both the inlet and outlet solutions. An absence of pH drift of the outlet solution is used as the criterion for system equilibration after each new temperature is reached.

A sample of the outlet solution is taken for analysis simply by changing the position of the 6-port sampling valve and rinsing the sample loop with acidified (HCl) deionized (DI) water. The sample solution and washings are caught in a volumetric flask. With experience, the appropriate size volumetric flask/sample loop volume ratio can be selected so that the calcium content of the diluted sample will fall within the range of the standards used to calibrate the Atomic Absorption (AA) Spectrophotometer. Standards and samples used in AA analysis each contain 4000 ppm Lanthanum (La), as suggested in the instrument manufacturer's (Instrumentation Laboratories) recommended procedures for calcium analysis when using air-acetylene flames. The test solution reservoir is a 52-gal glass-lined hot water heater with the heaters and the internal sacrificial anode removed. All fittings and tubing sections associated with the test solution reservoir are stainless steel (316 and 304). The high-pressure part of the system is plumbed with 1/8-in. or smaller Inconel-™600 tubing. The low-pressure part is plumbed with 1/4-in. stainless tubing.

PROCEDURE

This section explains the procedure followed in the preparation and treatment of test solutions, the start-up, and in normal operation.

PREPARATION AND TREATMENT OF TEST SOLUTIONS

Appropriate quantities of salts and deionized water were introduced into the feed tank. The solution was sparged with make-up gas for 1 to 2 hours. The feed tank system was then closed and the recirculation blower was activated to ensure the complete mixing and equilibration of makeup gas with the solution. The feed-tank-system gas pressure was slowly increased under continuous blower-driven circulation until the desired overpressure was achieved. A sample of feed-tank liquid was withdrawn for chemical analysis.

START-UP

Before the oven was turned on, appropriate valves were opened and closed to bypass the exposure chamber. The high-pressure feed pump was started. The pumping rate was adjusted to its maximum (about 8 mL/min), and the bypass system and sample valve plumbing was flushed until the outlet and inlet pH values were nearly the same. The pump stroke was then reduced so that flow rate was about 2 mL/min and the exposure chamber was valved in. The GC oven and associated circulating fan were then turned on, and the thermostat was set at a nominal 100°C. Approximately 45 minutes later, a steady pH reading was obtained from the outlet pH electrode. Tests of the flow rate versus the calcium content of the water verified that true equilibrium was achieved (see preliminary experiments and results). After another 45 to 60 minutes, an effluent sample was taken by appropriate manipulation of the six-port sampling valve; the sample's calcium content was determined later.

NORMAL OPERATION

After approximately two hours of operation at 100°C and sample acquisition, the thermostat was set to a nominal 125°C. Two hours were allowed to elapse, and effluent was sampled again. This process was continued at

25°C increments, until 300°C was reached. As the temperature was decreased, effluent samples were taken at 200°C, 150°C, and 100°C, after approximately 2 hours at each temperature setting. The oven was turned off after the final sampling, and the system was allowed to return to room temperature.

The feed tank was then refilled with the next test solution, and the whole process was repeated.

CHEMICAL ANALYSES

This section details the chemical analyses performed on the feed solution and the effluent solution.

FEED SOLUTION

The feed solution tank was sampled for CO_2 content and Cl^-, and/or HCO_3^-, as appropriate. The CO_2 sample was preserved in 1 N NaOH for later titrametric analysis. Chloride was determined using ion chromatography. Bicarbonate was determined titrametrically.

The CO_2 content of the feedwater is given with each data table and in most of the graphs. Because CO_2 is consumed in the calcite solubilization reaction:

$$CaCO_3(s) + CO_2(aq) + H_2O \rightleftarrows Ca^{2+} + 2HCO_3^- \qquad (1)$$

the CO_2 concentration of the equilibrated solution is: $[CO_2] = [CO_2]_{FW} - S$ where S is the molar solubility of calcite, the bracketed quantities are molar concentrations, and FW refers to feedwater. The molar bicarbonate ion concentration in each equilibrated solution is given by:

$$[HCO_3^-] = [HCO_3^-]_{FW} + 2S \qquad (2)$$

The fugacity of CO_2, which is needed for equilibrium calculations at each temperature and feedwater composition, can be estimated from the data of Ellis and Golding (1963).

EFFLUENT SOLUTION

The effluent-solution sample obtained from the HPLC valve sample loop was analyzed for calcium content using AA spectroscopy. All samples and standards aspirated into the AA nebulizer contained 4000 ppm La and 2% HCl. The linear working range was found to be 0 to 2 ppm Ca; therefore, samples were diluted appropriately to fall within this range.

PRELIMINARY EXPERIMENTS AND RESULTS

This section details the preliminary experiments made and the results obtained from these tests.

EFFECT OF FLOW RATE

Tests were performed at three different nominal temperatures, using demineralized water equilibrated with a nominal 5 psig overpressure of CO_2. It was important to establish the flow rate that would allow sufficient residence time in the calcite equilibration tube to ensure equilibrium. The highest flow rate that would result in chemical equilibrium was deemed desirable to shorten the interval between samplings after each new thermal equilibrium was established. Table 1 summarizes the results of flow-rate dependence tests. Samples were taken approximately 1 hour after either temperature or flow rate was changed.

At lower temperatures (~100°C), higher flow rates above 2.95 mL/min did not allow sufficient residence time to ensure chemical equilibrium. At higher temperatures (~300°C), higher flow rates yielded higher concentrations of Ca^{2+} in the effluent. (Analytical precision was only fair at the low calcium

TABLE 1. Flow-Rate Dependence Tests--Feedwater Was Deionized Water Equilibrated with 5 psig CO_2

Temperature °C	Pump Stroke Percent	Flow Rate, mL/min	Calcium Concentration Effluent, mg/L
106	20	1.10	174
105	40	2.95	173
104	70	5.60	156
103	100	8.15	155
150	20	1.10	78
149	40	2.95	78
148	80	6.47	80
149	100	8.15	79
313	20	1.10	0.79
313	40	2.95	1.1
312	70	5.60	1.4
308	100	8.15	1.9

concentrations encountered at 300°C). [Perhaps a wider temperature differential of the reactor column (colder at inlet) and high flow rate leads to a supersaturated state at the warmer column outlet, which did not equilibrate to saturation fast enough. At an intermediate temperature (~150°C), flow rate did not affect effluent Ca^{2+} concentration at least over the accessible range of flow rates.]

A pump stroke of 30% (2.0 mL/min) was chosen as the value to use in all subsequent experiments. This slow flow rate allowed long residence times in the reactor vessel and also led to a small temperature differential across the reactor equilibration zone.

From these flow-rate dependence tests and the experiences gained later in the test sequence, the most reliable data were believed to be those obtained in the 125° to 250°C temperature range. Fortunately, this temperature range included practical geothermal fluid temperatures where solubility data were the most relevant and were not available in the literature.

EXPERIMENTAL TEST AND RESULTS

The first test was done with deionized water equilibrated with CO_2(g) at a nominal 20 psia partial pressure at room temperature. The measured CO_2 concentration of the feedwater was 0.0368M. This test was performed to confirm that results obtained from the apparatus using the described procedure would adequately reproduce the data obtained by other investigators who had previously characterized this simple H_2O-CO_2-$CaCO_3$ system. The results are given in Table 2. A curve fit equation is also given in Table 2 to permit interpolation of the data.

Professor J. H. Weare (University of California - San Diego), using his computer model and data base based on the accepted accurate data of Ellis (1959), supplied predicted values of calcite solubility at 100°C, 150°C, and 200°C in the CO_2-H_2O matrix defined above. These values, designated as

TABLE 2. Calcite Solubility in Deionized Water Containing 0.0368M CO_2[a]

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L[b]
100.1	140
148.5	72
196	30
249	9.8
227	17
154	64
103.5	132
98.6	144
152.3	65
126.5	98

S(mg Ca/L) = 363.4 - 2.792 T + $0.0055T^2$ (T in °C)
r = 1.00

(a) Measured in feed solution at ambient temperature.

(b) Measured at ambient temperature.

Note: Data were obtained in the order given which is different from the standard routine outlined in the experimental section. This test emphasized obtaining good agreement with Dr. Weare's predicted values at 100°C, 150°C, and 200°C.

"previous work" in Figure 2, are superposed on the data from this work. These data are displayed graphically in Figure 2. The agreement is very good and verified that the test procedure gave reliably accurate values for calcite solubility.

TEST MATRIX

The solubility of calcite ($CaCO_3$) as a function of temperature was systematically investigated as a function of the variables NaCl, CO_2, and $NaHCO_3$. Specifically, calcite solubility as a function of temperature was measured in:

1. 1% NaCl, 3 levels of CO_2
2. 2% NaCl, 3 levels of CO_2
3. 5% NaCl, 3 levels of CO_2
4. 5 mM $NaHCO_3$ 2 levels of CO_2
5. 0.75 mM $NaHCO_3$ 2 levels of CO_2

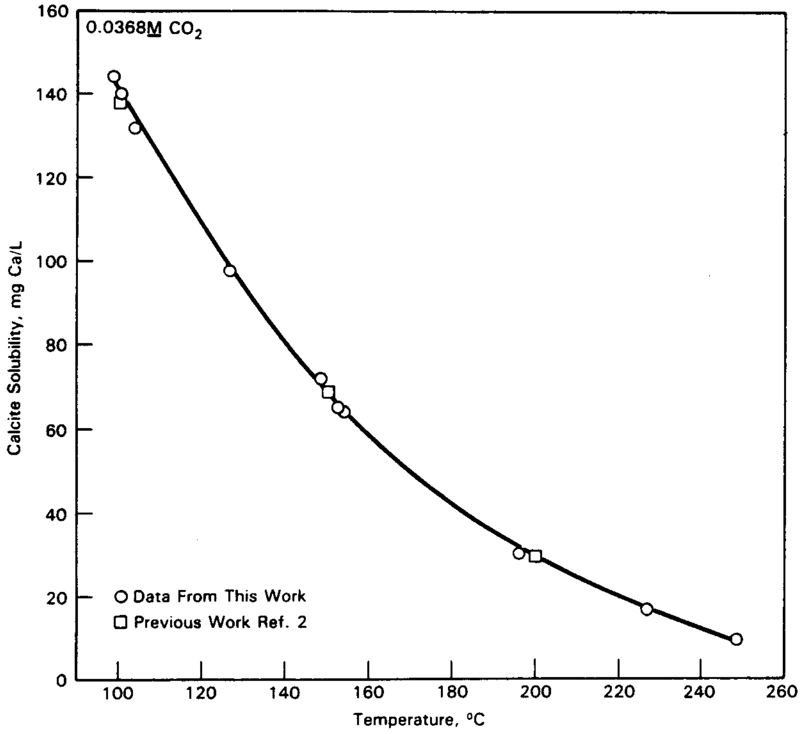

FIGURE 2. Calcite Solubility in Deionized Water

6. 3 mixtures containing different NaCl concentrations, 2 different $NaHCO_3$ concentrations, and 3 different CO_2 concentrations.

The above values of NaCl and $NaHCO_3$ are nominal; the actual values are shown in each table and graph. The solubility data are summarized in Tables 3 through 18 and are plotted in Figures 3 through 7. Also, the least squares regression equation is given for each data set in the tables to facilitate calculation of calcite solubility at any temperature in the 100° to 275°C range. Using the regression equations to predict solubility above approximately 275°C is not recommended.

TABLE 3. Calcite Solubility in 0.95% NaCl Solution Containing 0.00309 ± 0.0018 M CO_2[a]

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L[b]
100.1	61
119.8	55
149.3	46
172	37.5
197.5	25
223.5	20.8
247	13.8
272	9.7
290	8.3
197.8	26.2
152.6	44.5
96.6	64

S(mg Ca/L) = $112.52 - 0.5652T + 0.0006916T^2$ (T in °C)
$r = 1.00$
These data are displayed graphically in Figure 3.
(a) Measured in feed solution at ambient temperature.
(b) Measured at ambient temperature.

TABLE 4. Calcite Solubility in 0.98% NaCl Solution Containing 0.0375 ± 0.0007 M CO_2[a]

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L[b]
106.1	164
123.7	128
153.5	102
174.9	86.5
201	66.5
230	42.3
253	31
295	15.2
195	68.5
149.2	115
98.6	186

S(mg Ca/L) = $348.05 - 2.0605\ T + 0.0032\ T^2$
$r = 0.99$
These data are displayed graphically in Figure 3.
(a) Measured in feed solution at ambient temperature.
(b) Measured in ambient temperature.

TABLE 5. Calcite Solubility in 0.98% NaCl Solution Containing 0.0682 ± 0.0045 M CO_2[(a)]

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L[(b)]
98.5	218
123.4	162
150.4	125
175	97.5
200	73
226	54.5
251	38.6
276	25.8
300	16.3
195.6	76.5
99.6	206
145	125

$S(\text{mg Ca/L}) = 424.99 - 2.6133T + 0.0042T^2$ (T in °C)
$r = 1.00$

These data are displayed graphically in Figure 3.
(a) Measured in feed solution at ambient temperature.
(b) Measured at ambient temperature.

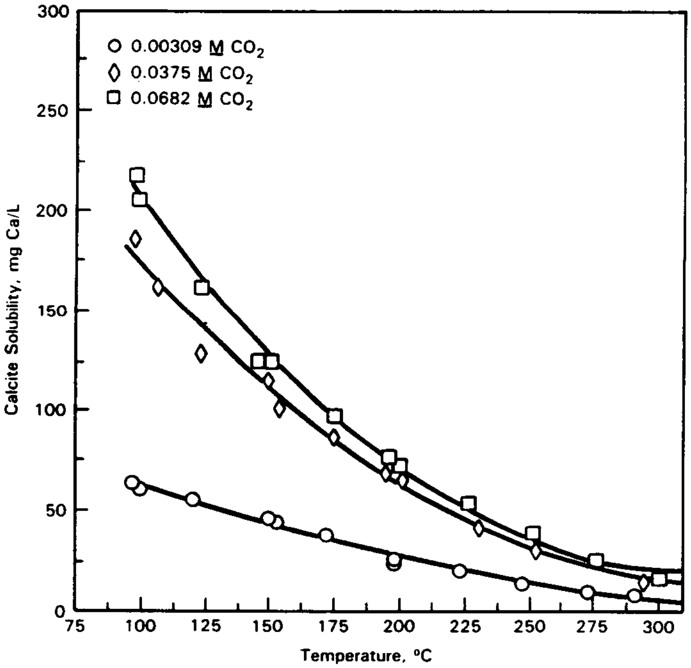

FIGURE 3. Calcite Solubility in Approximately 1% NaCl

TABLE 6. Calcite Solubility in 1.92% NaCl Solubility Containing 0.00386 ± 0.00011 M CO_2[a]

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L[b]
98.9	68
118.2	54.5
144.6	49
169.4	40
197.4	29.6
223.5	23.4
249	18
272	13.9
291	11.5
203	28

S(mg Ca/L) = $119.83 - 0.6269T + 0.000872^2$ (T in °C)
r = 1.00
These data are displayed graphically in Figure 4.
(a) Measured in feed solution at ambient temperature
(b) Measured in ambient temperature

TABLE 7. Calcite Solubility in 1.88% NaCl Solution Containing 0.0398 ± 0.0011 M CO_2[a]

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L[b]
100.2	200
125.1	168
150.4	125
174.8	100
197.7	73
225.6	62
250	44
274	28.4
298	18.6
198.4	79.5
147.2	137
96.3	224

S(mg Ca/L) = $417.03 - 2.4817T + 0.0039T^2$ (T in °C)
r = 1.00
These data are displayed graphically in Figure 4.
(a) Measured in feed solution at ambient temperature.
(b) Measured at ambient temperature.

TABLE 8. Calcite Solubility in 1.88% NaCl Solution Containing 0.0852 ± 0.0016 $\underline{M}$ CO_2(a)

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L(b)
96	276
121.8	202
147.5	153
174	127
197.1	96.5
226	74
250	43.6
275	36
297	26.6
197.0	95.5
151.1	162
100.6	260

$S(\text{mg Ca/L}) = 532.32 - 3.269T + 0.0053T^2$ (T in °C)
$r = 1.00$

These data are displayed graphically in Figure 4.

(a) Measured in feed solution at ambient temperature.

(b) Measured at ambient temperature.

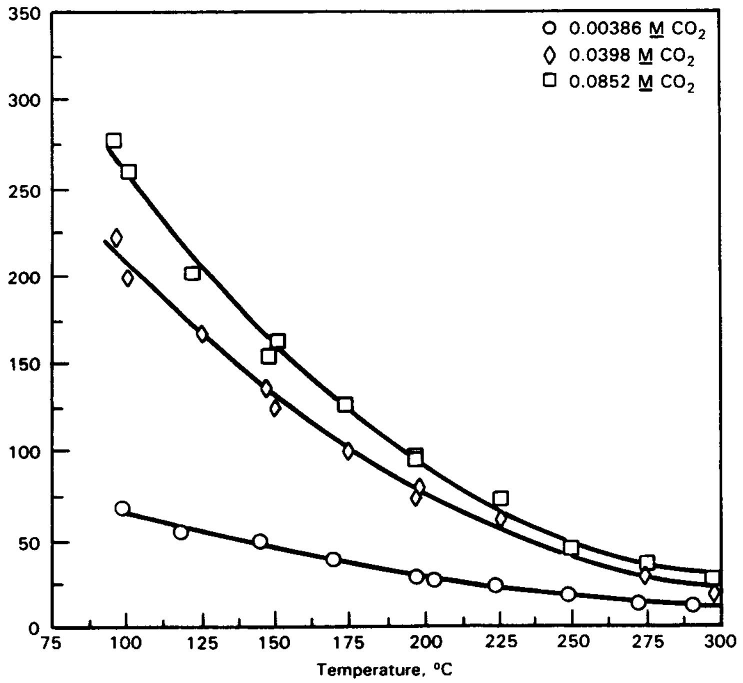

FIGURE 4. Calcite Solubility in 1.9% NaCl

TABLE 9. Calcite Solubility in 4.56% NaCl Solution Containing 0.00307 ± 0.00027 M CO_2[a]

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L[b]
98.0	76
114.9	70
144.4	63
168.0	51
201	37.6
225	32
248	27
272	23.2
293	19.5
202	37.6
149.5	61

S(mg Ca/L) = 128.95 - 0.5863T + 0.000715T^2 (T in °C)
r = 0.99
These data are displayed graphically in Figure 5.
(a) Measured in feed solution at ambient temperature.
(b) Measured at ambient temperature.

TABLE 10. Calcite Solubility in 4.78% NaCl Solution Containing 0.0423 ± 0.0014 M CO_2[a]

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L[b]
100.8	212
122.9	198
149.1	142
173.8	125
196.2	100
225	80.5
248	60.8
273	47.6
297	36
197.8	102.5
150.7	142
102.9	210

S(mg Ca/L) = 389.77 - 2.0221T + 0.0028T2 (T in °C)
r = 1.00
These data are displayed graphically in Figure 5.
(a) Measured in feed solution at ambient temperature.
(b) Measured at ambient temperature.

TABLE 11. Calcite Solubility in 4.78% NaCl Solution Containing 0.0984 ± 0.0011 M CO_2[(a)]

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L[(b)]
105.2	234
124.5	214
152.9	200
174.4	181
200	145
228	111
251	77
274	61
294	49
203	132
149.8	194
107.3	242

S(mg Ca/L) = 342.66 − 0.9478T − $0.000267T^2$ (T in °C)
r = 0.99

These data are shown graphically in Figure 5.

(a) Measured in feed solution at ambient temperature.

(b) Measured at ambient temperature.

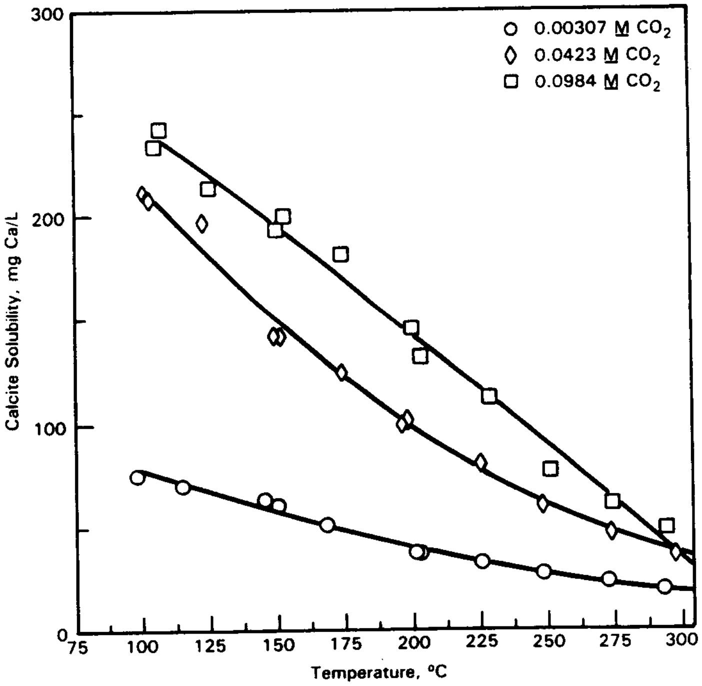

FIGURE 5. Calcite Solubility in 4.7% NaCl

TABLE 12. Calcite Solubility in 0.72 mM $NaHCO_3$ (44 mg HCO_3^-/L) Solution Containing 0.0373 ± 0.0016 M CO_2(a)

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L(b)
98.1	127
122.8	88
148.6	64
173.4	36
202	21
224	12
250	5
274	2
295	1
198.6	22
148.6	65
98.9	130

$S(\text{mg Ca/L}) = 313.58 - 2.3253T + 0.0043T^2$ (T in °C)
$r = 1.00$
These data are shown graphically in Figure 6.
(a) Measured in feed solution at ambient temperature.
(b) Measured at ambient temperature.

TABLE 13. Calcite Solubility in 0.75 mM $NaHCO_3$ (46 mg HCO_3^-/L) Solution Containing 0.0854 ± 0.0045 M CO_2(a)

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L(b)
97.1	174
121.5	129
148.6	82.4
172.5	47.0
202	28.7
222	17.6
250	7.4
272	3.0
292	0.8
203	27.3
150.4	65.2
100.9	139

$S(\text{mg Ca/L}) = 391.28 - 2.8925T + 0.0054T^2$ (T in °C)
$r = 0.99$
These data are shown graphically in Figure 6.
(a) Measured in feed solution at ambient temperature.
(b) Measured at ambient temperature.

TABLE 14. Calcite Solubility in 1.98% NaCl, 0.72 mM $NaHCO_3$ (44 mg HCO_3^-/L) Solution Containing 0.0346 ± 0.0057 M CO_2[a]

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L[b]
101.1	214
126.3	156
152.4	114
177	95
204	69
226	53.2
253	35.5
276	24.2
304	14.1
206	70
152.4	119
103.6	196

$S(\text{mg Ca/L}) = 419.85 - 2.5648T + 0.0041T^2$ (T in °C)

$r = 1.00$

These data are displayed graphically in Figure 6.

(a) Measured in feed solution at ambient temperature.

(b) Measured in ambient temperature.

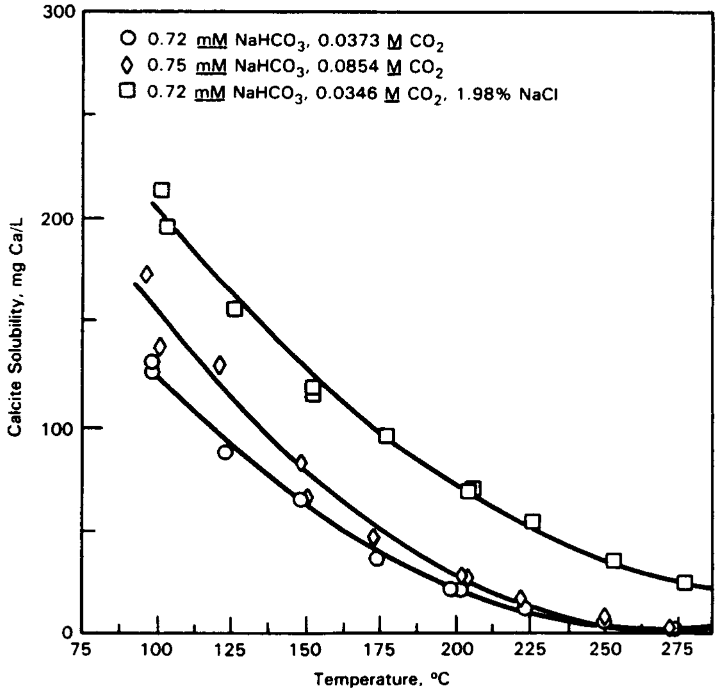

FIGURE 6. Calcite Solubility in 0.7 mM $NaHCO_3$

TABLE 15. Calcite Solubility in 5.15 mM $NaHCO_3$ (314 mg HCO_3^-/L) Solution Containing 0.0375 ± 0.006 M CO_2(a)

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L(b)
99.2	74.2
124.2	40.9
151.4	20.7
175.6	9.6
202	3.6
223	1.4
251	0.5
274	0.2
294	0.2
201	3.6
148	24.2
97.4	87.1

$S(\text{mg Ca/L}) = 225.75 - 1.9209T + 0.004T^2$ (T in °C)

$r = 0.98$

These data are displayed graphically in Figure 7.

(a) Measured in feed solution at ambient temperature.

(b) Measured at ambient temperature.

TABLE 16. Calcite Solubility in 5.20 mM $NaHCO_3$ (317 mg HCO_3^-/L) Solution Containing 0.0867 ± 0.0068 M CO_2(a)

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L(b)
100.2	110
123.5	70
150.5	33.5
174.5	15.8
202	6.2
224	2.5
252	0.7
276	0.5
302	0.15
202	6.2
147.7	35.5
96.2	121

$S(\text{mg Ca/L}) = 316.12 - 2.623T + 0.0053T^2$ (T in °C)

$r = 0.99$

These data are displayed graphically in Figure 7.

(a) Measured in feed solution at ambient temperature.

(b) Measured at ambient temperature.

TABLE 17. Calcite Solubility in 0.93% NaCl, 5.53 mM $NaHCO_3$ (337 mg HCO_3^-/L) Solution Containing 0.0849 + 0.0057 M CO_2[a]

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L[b]
104	172
127.8	116
153.4	68.7
178.6	39.2
203	26.5
226	14
253	6
277	2.4
306	0.4
206	24
152.4	88
105.1	188

S(mg Ca/L) = $476.7 - 3.6185T + 0.0068T^2$ (T in °C)
r = 0.99
These data are displayed graphically in Figure 7.
(a) Measured in feed solution at ambient temperature.
(b) Measured at ambient temperature.

TABLE 18. Calcite Solubility in 4.82% NaCl, 6.62 mM $NaHCO_3$ (404 mg HCO_3^-/L) Solution Containing 0.0704 ± 0.0023 M CO_2[a]

Temperature, °C	$CaCO_3$ Solubility, mg Ca/L[b]
102.4	244
123.5	184
148.9	135
174.1	99
202	61
225	40.5
252	24.5
276	15.2
303	7.0
198.2	62
149.4	139
101.8	240

S(mg Ca/L) = $553.19 - 3.7375T + 0.0064T^2$ (T in °C)
r = 1.00
These data are displayed graphically in Figure 7.
(a) Measured in feed solution at ambient temperature.
(b) Measured in ambient temperature.

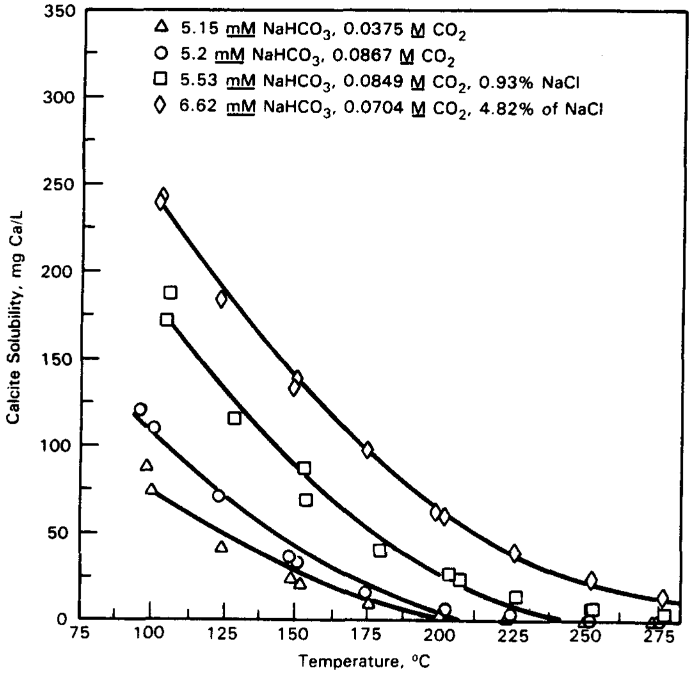

FIGURE 7. Calcite Solubility in 5 mM $NaHCO_3$

ERROR ANALYSIS - ESTIMATED UNCERTAINTIES IN REPORTED VALUES

The following experimentally measured quantities affected the ultimate results reported:

1. temperature
2. calcium concentration of diluted system effluent samples
3. CO_2 content of feedwater
4. salt (NaCl and $NaHCO_3$) content of feedwater.

For each sample taken from the system, the temperature reported was taken as the measured value at the calcite equilibration-tube effluent. The thermocouple used and the readout device were calibrated by the Standards Laboratory at the Hanford Engineering Development Laboratory. At 100°C, the temperature-measuring system used indicated 100.4°C; at 204°C, the system indicated 206°C; and at 314°C, the system indicated 317°C. Corrections were applied to raw temperature measurements and were included in tabulated values.

The accuracy of the analytical results was estimated to be ± 2% in most cases. However, for those samples where the calcium concentration of effluent was low (<10 ppm), the relative uncertainty was greater. The sampling procedure used to obtain samples of feedwater for CO_2 analyses was not entirely satisfactory. Great care was needed to ensure negligible loss of CO_2 during sampling, especially for those tests where feedwater was equilibrated with 35 to 40 psia $CO_2(g)$. Values of CO_2 concentration given in the tabulated results may be biased on the low side but these cannot be quantified with any confidence.

DISCUSSION OF RESULTS

Solubility of calcite depends on the temperature and chemical composition of a solution in contact with it. The most important solutes from a geothermal viewpoint are CO_2, HCO_3^-, and dissolved salts, primarily NaCl. The pH has a major influence on calcite solubility, but pH in geothermal brines is controlled by the CO_2-HCO_3^- equilibrium. The results in this report are given on the basis of CO_2 and HCO_3^- content of feedwater only.

Of the variables considered in this study, temperature and bicarbonate ion concentration had the largest effects on calcite solubility. The well-known retrograde temperature coefficient of calcite solubility was apparent from the results of all feedwater compositions tested. Bicarbonate ion tends to suppress calcite solubility as predicted from the solubilization reaction.

$$CaCO_3(s) + CO_2(aq) + H_2O \rightleftarrows Ca^{2+} + 2HCO_3^- \qquad (3)$$

As Equation 3 indicates, CO_2 fugacity also affects calcite solubility. CO_2 fugacity is dependent on both the temperature and the concentration of dissolved salts in the solution. These dependencies were well established in the work published by Ellis and Golding (1963). Qualitatively, for a given feedwater composition at room temperature, CO_2 fugacity increases up to approximately 175°C and decreases above this temperature. (This behavior was expected under the conditions realized in the tests reported in this report; i.e., no separate gas phase was present in the equilibration chamber). For a given CO_2

overpressure on feedwater, the higher the salt content is, the higher the CO_2 fugacity will be at any temperature. This "salting out" effect is a characteristic of many salt solution-gas systems.

Finally, there is the salt-effect or activity effect on the calcite solubility product equilibrium constant. The qualitative trend accompanying this phenomenon leads to an increased calcite solubility and an increasing salt content of the dissolving solution.

Detailed, quantitative treatment of all the factors and effects mentioned above is beyond the scope and purpose of the work described in this report.

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2. Ellis, A. J. 1959. "The Solubility of Calcite in Carbon Dioxide Solutions." Amer. J. of Sci., 257:354-365.

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