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Field Tests to Determine Scaling Tendency of Some Moderate-Temperature Geothermal Brines

R. J. Robertus
R. G. Sullivan
D. W. Shannon

September 1986

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

PNL-5991

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
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**FIELD TESTS TO DETERMINE SCALING
TENDENCY OF SOME MODERATE-TEMPERATURE
GEOTHERMAL BRINES**

R. J. Robertus
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PNL--5991

DE86 016089

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SUMMARY

Several field tests were completed to determine the scaling tendency of moderate-temperature geothermal brines. Data were taken on the Heber as well as the East Mesa Known-Geothermal-Resources-Areas (KGRA's). The test results most directly benefit the Heber Geothermal Binary Demonstration Plant, but some have been generalized to be useful for other moderate-temperature (302-460°F [150-239°C]) geothermal reservoirs also.

Field experiments determined conditions under which calcite, silica, and metal sulfides are likely to form. The calcite tests determined pressures which must be maintained to prevent gas-breakout and ensuing calcite deposition. Required pressures varied from one reservoir to the next and were strong functions of non-condensable gas content.

The brine cooling tests tried to quantify the amount of silica which would drop out of the Heber brine by incrementally cooling it below a design set point of 150°F (66°C). The conclusion was that no detectable increase in silica occurred in times relevant to plant operations when the brine was cooled to 120°F (49°C).

Although the cooling tests showed no detectable increase in silica formation, other materials did form in small amounts. The list includes magnetite (Fe_3O_4), calcite (CaCO_3), and mixtures of lead, zinc, and arsenic sulfides. Even for the lowest outlet temperature (120°F) the particulate loading increased only about 50% over inlet conditions. Thus, for the Heber brines, the majority of material entering an injection well comes in the form of sand from the production wells. This same conclusion was supported by earlier work on the East Mesa KGRA.

ACKNOWLEDGMENTS

We would like to acknowledge the assistance of Paul Thrash and Tony Adduci of the U.S. Department of Energy who provided administrative help so the work could be done. Their efforts secured financial support of the U.S. Department of Energy.

The cooperation of many staff of the San Diego Gas and Electric Company at the Heber Geothermal Binary Demonstration Project were needed to complete the work. Key supporters were Tiff Nelson, Kyle Taylor, Jim Ludolph, Henry Castanieto, and Gil Lombard of San Diego Gas and Electric Company. Richard Pilsbury of Westec Inc. provided technicians and other craft people when needed.

The cooperation of Dennis Downs and Jeff Brown of Magma Electric Company is also gratefully acknowledged.

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1.0 INTRODUCTION

In general the causes of calcite (CaCO_3), silica (SiO_2) and sulfide scaling are understood in simple water systems. Scale control in a geothermal plant, however, requires understanding the behavior of many minor elements in highly complex brines. Interactions of silica, calcium and CO_2 with the brine temperature, pressure, and time after production must be known and understood for optimal plant operation.

Moderate temperature reservoirs are seen as most compatible with binary cycle plants where the geothermal brine gives up its energy by passing through a series of heat exchangers. Spent brine is then injected into underground formations. Solids which form and remain on heat exchanger surfaces will decrease plant performance by reducing heat transfer coefficients. Particles which form but remain suspended in the brine pose potential plugging problems for injection wells.

One common form of scale in geothermal plants is calcite. It forms when carbon dioxide is released from the brine and the brine becomes supersaturated in calcium carbonate. Although the thermodynamics of calcite formation is fairly well understood, no reliable methods exist for predicting when flashing and resulting precipitation will occur in geothermal brines. Pumping costs to keep all the CO_2 in solution add directly to the cost of geothermal power. Generally pressures are kept some "safe" limit above what is thought necessary to prevent breakout. If actual breakout conditions were known, pumping costs could be held to a minimum, and no calcite would form.

Silica particles are known to form in flash plants using high temperature geothermal fluids ($>465^\circ\text{F}$ [240°C]). The material is concentrated, filtered and eventually removed from flash plants as a solid residue. The collection and disposal processes are available on a commercial scale for flash plants and high temperature brines. In contrast little work has been done on moderate temperature brines from 302 to 462°F (150 to 239°C) coupled to binary cycle plants. The chemistry of silica deposition is highly complex (Iler 1979). No simple rate expression exists for predicting silica formation in complex brines at moderate temperatures. Diffusion, polymerization and crystal growth are all

involved in ways that depend on pH and salinity as well as temperature. The rate of formation of silica is known to be slow at modest temperatures unless the supersaturation ratio is high. In order to determine the effect of brine cooling as it relates to silica precipitation and potential injection well plugging, one must run tests using the actual brine in question.

Sulfide scales are expected to form on cooling since most known geothermal sulfide species show decreased solubility with temperature. Thermodynamic data allow calculation of equilibrium yields for the sulfide scales, but kinetic information is largely missing. Rates must again be determined experimentally.

2.0 CONCLUSIONS

The following conclusions are based on field tests at two moderate temperature geothermal reservoirs; East Mesa and Heber. The information is most relevant for binary cycle plants coupled to the brines. Most results can be extrapolated to other moderate temperature reservoirs with only minor qualifications. A few findings would be important to flash plants also.

- Calcite scaling can be stopped by maintaining pressures above experimentally determined gas breakout pressures.
- Gas breakout data must be determined experimentally because analytical data needed to predict it is rarely accurate enough.
- Silica formation/scaling is unlikely to cause problems because the kinetic reactions are so slow at binary plant operating conditions at moderate temperature reservoirs.
- Sulfide scales are thermodynamically favored to form in most plants. Total amounts which do form and remain in suspension are small relative to suspended sand particles which come up the production wells.
- The amount of sulfide scale which might form on heat transfer surfaces was not measured.

3.0 GAS BREAKOUT TESTS

The gas breakout equipment was designed and built to provide operating information for the Heber Binary Cycle Demonstration Plant. Preliminary testing was completed on the East Mesa KGRA to establish good operating procedures. Results are presented for both series of tests.

3.1 EQUIPMENT DESCRIPTION

The equipment shown isometrically in Figure 3.1 is mounted on three skids. One contains the actual breakout equipment. A second contains recording instrumentation. The third supports an air-cooled heat exchanger for cooling circulating water. If plant cooling water is available, the air-cooled heat exchanger can be eliminated. The entire system is designed to be easily transportable and operable at remote locations. The only additional item required is a power source to run the cooler and instrumentation. Portable generators can be used at actual well sites if electrical line power is not available.

A flow diagram for the equipment is shown in Figure 3.2. During operation brine flows through an inlet heat exchanger (and/or by-pass) into an adjustable orifice/sight glass assembly, to a gas collection chamber, then on to an exit heat exchanger. Brine flow is controlled using valve V-4 at the exit of the gas collection chamber. Brine temperature at the sight glass is varied by changing the by-pass rate of hot inlet brine around the first heat exchanger. Valves V-2 and V-6 are used. The adjustable orifice, sight glass assembly is the producer and detector of gas breakout from the brine. For any given temperature of the brine, pressure is dropped across the needle valve until bubbles of gas are detected in the sight glass. The bubbles are detected by eye and also by a light source/photoelectric cell combination.

Temperatures are measured at points shown using certified type K thermocouples. Pressures are measured with calibrated pressure transducers. All temperature and pressure readings are sent to a data logging system. The data-logger paper tape output serves as the permanent record.

FIGURE 3.1. Isometric View of Gas Breakout Equipment

FIGURE 3.2. Gas Breakout Test System

The recorder trace from the photoelectric cell is used as an operational guide to be sure the same bubbling conditions are selected at each temperature/pressure point. Figure 3.3 shows a trace of the recorder output from part of one test. The pressure drop across the needle valve would successively generate transparent waves, very fine bubbles, and then large bubbles. The pressure at which very fine (mist like) bubbles formed was taken as the gas breakout point. The difference in pressure going from waves to mist was typically 2 to 4 psi.

Other strip chart recorders monitor temperature and pressure just before and just after flashing. These recorders serve as operational guides only. One additional recorder monitors pressure drop across an orifice. This is the flow indicator and provides the operator visual indication of his desired control point. Optionally a turbine flow meter with its own readout electronics was used as a flow measuring device.

3.2 EXPERIMENTAL RESULTS

Meaningful results can be achieved only when the brine to this test stand is unflashed. Hence, any wells being tested must be pumped.

Two tests were completed on the system at the East Mesa KGRA. The purpose of the first test were to verify that all the equipment and instrumentation was operational. Pressure transducers were calibrated against a Hiese gauge which was checked in a standards laboratory just before the tests. Thermocouples were accompanied by calibration certificates from the vendor. A certified turbine flow meter was used to calibrate the orifice.

Initial attempts to get breakout information were only partially successful. The point of incipient breakout was determined by eye and thus became somewhat subjective. (The photoelectrical cell was installed later.) Data was a bit scattered and discrepancies were not resolved immediately.

A second test was run later after a photoelectric cell was installed on the sight glass. This light detection set-up proved more reliable than the eye. After one breakout point was established visually, it was simple to come back to exactly the same conditions at other temperatures and pressures.

FIGURE 3.3. Output from Photoelectric Cell

The first two tests were done at the inlet to a geothermal power plant rather than a single well. The sampled stream was a composite of four different wells in the East Mesa KGRA. This location was chosen because power and tools were convenient.

Results from the second test are shown in Figure 3.4. The smooth "misty flow (experimental)" curve indicates that data are probably consistent. The same plot shows pressure temperature data for water as a reference point. Also shown are calculated curves. One calculation uses Henry's law constants for CO_2 solubility in pure water. It simply treats all of the CO_2 in solution as H_2CO_3 . Disassociation reactions are ignored. So are effects of ionic strength.

FIGURE 3.4. Experimental vs Calculated Breakout Pressures at East Mesa

3 The second calculated curve is from a sophisticated chemical equilibrium computer code which is developed specifically for complex solubility calculations. The code's acronym is CHMTMP, and it was developed internally at Pacific Northwest Laboratory. This code considers several disassociation reactions for CO_2 in solution. It also accounts for mineral precipitates which could consume CO_2 . The data base for the code includes 8 gases, 187 minerals, and 200 aqueous species. It uses a Gibbs free energy minimization to calculate concentrations at equilibrium. The data base was current in 1981 so its predictions are considered as accurate as present data and calculational techniques will allow. One limitation for geothermal applications is that no hydrocarbon gases are considered. Hydrocarbons, especially methane, exist in geothermal brines.

Comparison of theoretical and calculated values shows there is still a need to run experiments. The agreement between CHMTMP and experiment at 77°C is artificial. The code used this as a reference point to set the chemistry of the brine. Deviations between the code and experiment at higher temperatures cannot be completely explained. Experimentally we had to get to lower pressures than the code predicted. Part of the explanation could be kinetic effects which might not allow immediate bubble formation at equilibrium conditions.

Figure 3.5 provides more information on the experimental versus computed data. The CHMTMP total pressure line is the total equilibrium pressure in the system including water's vapor pressure. The CO_2 partial pressure line is partial pressure of CO_2 only. The implication here is that gas bubbles which do form at high temperatures contain significant amounts of water vapor. They are not pure carbon dioxide. (Other noncondensable gases were ignored in the calculations).

Three different breakout tests were run on the Heber brines. The first was on brine from a single well, the second on combined flow from two wells and the third on combined flow from 5 wells. Figure 3.6 shows a single curve for the Heber brine. Within the accuracy of the instruments being used, there were no differences in the three tests. Figure 3.6 also compares breakout curves for the East Mesa and Heber brines. Notice the large difference in pressure

FIGURE 3.5. Equilibrium vs Experimental Values at East Mesa

FIGURE 3.6. Comparison of Gas Breakout Pressures at Heber and East Mesa

(at any given temperature) which must be maintained to keep gases in solution in the East Mesa brine. Also notice how close the Heber brines are to the pure water curve.

3.3 THEORETICAL ASPECTS OF GAS BREAKOUT

Ideally one would like to be able to predict gas breakout conditions using relatively simple mathematics and routine chemical analyses such as presented in Table 3.1. The development which follows relies on pH and Ca^{++} analysis to predict CO_2 partial pressure. The calculation first uses the chemical analyses to predict a high temperature pH. Knowing how pH varies with temperature, we can then predict changes in CO_2 partial pressure with temperature. Both calculational procedures use equilibrium relationships for the following reactions

$\text{CO}_2(\text{g}) = \text{partial pressure in ATM}$

The last reaction is included because calcite (CaCO_3) is known to form scale when CO_2 gas is released from certain brines. Preventing calcite scale formation depends on keeping the CO_2 gas in solution.

Step 1. Calculate Brine pH at Well Conditions

Given the following analytical data for Heber brine

TABLE 3.1. Analyses of Heber and East Mesa Geothermal Fluids

Date Location	Sept. 84 East Mesa Inlet Combined 4 Wells	Heber				Plant Inlet Best or Available
		16-May-85 Plant Inlet Well 4	21-May-85 Plant Inlet Well 462	21-Sept-85 Plant Inlet Wells 1 & 3-6	12-Dec-85 Plant Inlet Wells 1-6	
pH	5.7	5.5	NA	5.4	5.3	5.3 @ 80F
Conductivity		NA	NA	NA	21400	21400
		mg/l	mg/l	mg/l	mg/l	0
CL ⁻	3449	7730	8020	7760	7790	7825
SO ₄ ⁼	70	82	69	57	85	73
HCO ₃ ⁻	490	40.5	28	42	30.6	35
CO ₂ (total)	1738	164	124	131		150
H ₂ S				0.47		0.47
Al	<0.1	<0.1	<0.1	<0.2	<0.2	<0.1
Ca	51.5	806	807	956	967	884
Cu	1.1	<0.01	<0.01	<0.01	<0.01	0
Cr	<0.01	<0.01	<0.01	<0.01	0.05	0.05
Fe	15.5	0.86	0.95	2.6	1.2	1.0
K	210	276	297	360	325	314.5
Mg	1.8	1.7	1.6	2.2	3.1	2.15
Na	1085	4070	4170	3600	4400	4060
Ni	<0.01	<0.01	<0.01	0.01	0.06	0.06
Si	103	97	99	106	111	103
Sr	11.7	35	34	32	27	32
Zn	<0.05	<0.05	<0.05	0.2		0.2
Ag		<0.01	<0.01	<0.02		<0.02
As		0.14	0.14	0.19	0.26	0.18
B		4.6	4.8	4.8	4.1	4.58
Ba		3	3.2	3.3	3.1	3.15
Cd		0.05	0.01	0.02	0.02	0.03
Li		6.9	7.2	6.5	9.2	7.45
Mn		0.16	0.14	0.2	0.28	0.20
Pb					0.19	0.19
Sb		0.016	0.019	0.1		0.05
Sn					0.25	0.25

Total carbon as $\text{CO}_2 = 150 \text{ ppm}$

pH @ $80^\circ\text{F} = 5.3$ (measured with in-line pH cell before gases escaped)

$\text{Ca}^{++} = 806 \text{ mg/liter} = 0.0201 \text{ moles/Kg}$

Non-Condensable Gas Weight = $8.6 \text{ ppm @ } 150^\circ\text{F}$

Reservoir temperature = 360°F

We can observe that

$$\text{Total Carbon} = C_{\text{CO}_2(\text{g})} + C_{\text{H}_2\text{CO}_3(\text{aq})} + C_{\text{HCO}_3^-} + C_{\text{CO}_3^{=}} \quad (3.3.5)$$

This total carbon number will not change so long as no calcite precipitates and all $\text{CO}_2(\text{g})$ remains in the system.

If all concentrations are expressed as g-moles/ KgH_2O , then we must know the total volume and composition of noncondensable gas/ KgH_2O in order to evaluate $C_{\text{CO}_2(\text{g})}$.

Assume the non-condensable gases are ideal. Then the number of moles of CO_2 can be expressed as

$$C'_{\text{CO}_2} = \frac{N_{\text{CO}_2}}{V_{\text{NC}}} = \frac{P_{\text{CO}_2}}{RT} = \frac{P_{\text{TOT}} Y_{\text{CO}_2}}{RT} \quad (3.3.6)$$

where C'_{CO_2} = Moles CO_2 /liter gas

P_{CO_2} = Partial pressure CO_2 gas

V_{NC} = Volume of noncondensable gas

R = Gas constant

T = Kelvin temperature

P_{TOT} = Total inert gas pressure

Y_{CO_2} = Mole fraction CO_2 in inert gas.

Let V^α = liters gas/Kg brine. Then

$$C_{\text{CO}_2} = C'_{\text{CO}_2} * V^\alpha = \frac{P_{\text{CO}_2}}{RT} V^\alpha \quad (3.3.7)$$

Since concentrations are related to activities by the activity coefficient, we can write $\gamma_i C_i = []_i$ where γ_i = activity coefficient for species i . From Reactions 3.3.1 to 3.3.5 we can write (using Equation 3.3.7 also)

$$\begin{aligned}
 \text{Total Carbon} &= P_{\text{CO}_2} \frac{V^\alpha}{RT} + \frac{[\text{HCO}_3^-][\text{H}^+]}{\gamma_{\text{H}_2\text{CO}_3} K_2} + \frac{[\text{CO}_3^{=}] [\text{H}^+]}{\gamma_{\text{HCO}_3^-} K_3} + \frac{K_{\text{SP}}}{\gamma_{\text{CO}_3^{=}} [\text{Ca}^{++}]} \quad (3.3.8) \\
 &= \frac{V^\alpha}{RT} \frac{[\text{CO}_2(\text{aq})]}{K_1} + \frac{[\text{CO}_3^{=}] [\text{H}^+][\text{H}^+]}{\gamma_{\text{H}_2\text{CO}_3} K_2 K_3} + \frac{K_{\text{SP}} [\text{H}^+]}{[\text{Ca}^{++}] \gamma_{\text{HCO}_3^-} K_3} + \frac{K_{\text{SP}}}{\gamma_{\text{CO}_3^{=}} [\text{Ca}^{++}]} \\
 &= \frac{V^\alpha}{RT} \frac{[\text{HCO}_3^-][\text{H}^+]}{K_1 K_2} + \frac{K_{\text{SP}} [\text{H}^+][\text{H}^+]}{[\text{Ca}^{++}] \gamma_{\text{H}_2\text{CO}_3} K_2 K_3} + \frac{K_{\text{SP}}}{[\text{Ca}^{++}] \gamma_{\text{HCO}_3^-} K_3} + \frac{K_{\text{SP}}}{\gamma_{\text{CO}_3^{=}} [\text{Ca}^{++}]} \\
 &= \frac{K_{\text{SP}}}{[\text{Ca}^{++}]} \frac{V^\alpha}{RT} \frac{[\text{H}^+][\text{H}^+]}{K_1 K_2 K_3} + \frac{[\text{H}^+]^2}{\gamma_{\text{H}_2\text{CO}_3} K_2 K_3} + \frac{\text{H}^+}{\gamma_{\text{HCO}_3^-} K_3} + \frac{1}{\gamma_{\text{CO}_3^{=}}} \quad (3.3.8)
 \end{aligned}$$

The parameter V^α is difficult to predict but can be measured experimentally. For the Heber brine a "best value" was considered to be 8.6 ppm @ 150°F. If pressure is constant this value will change with temperature as more CO_2 is released from the brine. Gas analyses at Heber show the CO_2 is only 10% of the total gas at 150°F, 1 atm. That percentage is probably higher at wellhead conditions but for a first approximation we will assume V^α varies as an ideal gas with temperature. (This assumption is probably not valid for East Mesa Brines because CO_2 content is higher and its solubility changes significantly with temperature.)

$$\text{Thus } V^\alpha = \frac{8.6 \times 10^{-3} \text{ g}}{\text{Kg Brine}} \left| \frac{\text{mole}}{28 \text{ g}} \right| \frac{22.4 \text{ l}}{\text{mole}} \left| \frac{(150 - 32)/1.8 + 273}{273^\circ \text{K}} \right| = 0.80 \times 10^{-3} \text{ liters/kg}$$

Where 28 g/mole is the approximate gas mixture molecular weight

$$\text{@ } 360^\circ \text{F } V^\alpha = \frac{0.80 \text{ liter} \times 10^{-3}}{\text{kg}} \times \frac{14.7 \text{ psia}}{153 \text{ psia}} \times \frac{(360 + 460)}{(32 + 460)} = 0.13 \times 10^{-3} \text{ liter/kg}$$

Note: 153 psia is the vapor pressure of pure water @ 360°F. Well pumps boost the pressure closer to 200 psia at Heber. The real pressure down hole was unknown so this value for V^a is approximate.

In order to calculate the high temperature pH using Equation 3.3.8, we must have equilibrium data and activity coefficients for all species.

Table 3.2 lists polynomial coefficients for calculating equilibrium data from equations of the form

$$\pm \log_{10} (K_{eq}) = C0 + C1*T + C2*T^2 + C3*T^3 + C4*T^4$$

With T in °C

Data for calcite were taken from Morrey, 1978. Other constants were determined using a regression analyses of data given by Cobble, 1982. Table 3.3 shows the equilibrium constant values at temperatures of possible interest to the Heber plant. Activity coefficients given in Table 3.4 were taken from unpublished in-house graphs which are fast and easy to use. The graphs were generated using the equations in Appendix A. The tabular values may not agree exactly with the calculated ones due to interpolation errors in reading the graphs.

TABLE 3.2. Polynomial Coefficients for Selected Carbon Containing Reactions

Reaction	C0	C1	C2	C3
$\text{CaCO}_3 \rightarrow \text{Ca}^{++} + \text{CO}_3^{--}$	-8.19243	-0.006127	-5.77882E-05	4.15442E-08
Note: we get pK values below				
$\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{aq})$	1.22	0.01461	-6.72000E-05	8.74500E-08
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HCO}_3^-$	6.524	-0.00667	6.29300E-05	-6.4500E-08
$\text{HCO}_3^- \rightarrow \text{CO}_3^{--} + \text{H}^+$	10.598	-0.01141	7.63100E-05	-8.07100E-08

TABLE 3.3. Calculated Equilibrium Constants for Selected Carbon Containing Reactions at Conditions Relevant to the Heber Plant

Temp	°F	77	120	130	150	350	360
	°C	25.0	48.9	54.4	65.6	176.7	182.2
$\text{CaCO}_3 \rightarrow \text{Ca}^{++} + \text{CO}_3^{--}$		4.16E-09	2.37E-09	2.04E-09	1.48E-09	1.41E-11	1.06E-11
$\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{aq})$		3.58E-02	2.06E-02	1.85E-02	1.53E-02	8.17E-03	8.28E-03
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HCO}_3^-$		4.02E-07	4.56E-07	4.60E-07	4.58E-07	1.11E-07	9.83E-08
$\text{HCO}_3^- \rightarrow \text{CO}_3^{--} + \text{H}^+$		4.37E-11	6.12E-11	6.46E-11	6.99E-11	3.03E-11	2.73E-11

TABLE 3.4. Activity Coefficients for Species Involved in Calcite Precipitation

	77	120	130	150	350	360
Ca ⁺⁺	0.292	0.281	0.279	0.27	0.18	0.175
H ₂ CO ₃	1.114	1.113	1.11	1.111		1.112
HCO ₃ ⁻	0.71	0.692	0.69	0.688		0.6001
CO ₃ ⁼	0.225	0.215	0.205	0.201		0.121

In order to calculate a reservoir pH we will assume the total carbon and Ca⁺⁺ are values equilibrated at reservoir temperatures near 360°F. Substituting known values into Equation 3.3.8, we get

$$\begin{aligned}
 C_{\text{Total}} &= \frac{150 \text{ g}}{10^6 \text{ g H}_2\text{O}} = \frac{0.150 \text{ g}}{\text{Kg}} \left| \frac{1 \text{ g mole}}{44 \text{ g}} \right| = 3.4 \times 10^{-3} \frac{\text{g moles}}{\text{Kg}} \\
 &= \frac{1.06 \times 10^{-11}}{(0.175)(0.0201)} + \frac{0.13 \times 10^{-3}}{(0.0821)(455)} + \frac{[\text{H}^+][\text{H}^+]}{8.28 \times 10^{-3} \cdot 9.83 \times 10^{-8} \cdot 2.73 \times 10^{-11}} \\
 &\quad + \frac{[\text{H}^+][\text{H}^+]}{1.112 \times 9.83 \times 10^{-8} \cdot 2.73 \times 10^{-11}} \\
 &\quad + \frac{[\text{H}^+]}{0.6001 \times 2.73 \times 10^{-11}} \\
 &\quad + \frac{1}{0.121}
 \end{aligned}$$

This can be rearranged to the form

$$a\text{H}^{+2} + G\text{H}^+ + C = 0$$

For which the solutions are

$$[\text{H}^+] = \frac{-G \pm \sqrt{G^2 - 4aC}}{2a}$$

Solving gives $[\text{H}^+] = 5.88 \times 10^{-6}$ or pH = 5.73 @ 360°F.

Other methods exist for estimating high temperature brine pH values. Henely (1984) develops a salinity/pH relationship based on K-feldspar and albite (both silica minerals) going to K-mica. Using formulas outlined by him. One calculates a pH of 5.80 for the brine at 200°C. This did not seem too unreasonable except the same formulas predicted a pH value of 6.8 at 100°C. The value of 6.8 at 100°C is not consistent with experimental measurements close to that temperature. Hence, details of the silica equilibrium as they relate to pH are omitted here.

The difference in pH going from wellhead to plant outlet is predicted to increase about 0.4 pH units. For purposes of predicting CO₂ breakout pressures letting pH vary linearly with temperature between 360°F @ 80°F seems reasonable. This is true for the Heber brine but not in general for geothermal brines.

Step 2. Calculate Gas Breakout Pressures

To predict CO₂ breakout pressures at different temperatures it is convenient to rearrange Equation 3.38 as

$$P_{CO_2} \frac{V^a}{RT} = C_{TOT} - \frac{K_{SP}}{[Ca^{++}]} \frac{[H^+]^2}{\gamma_{H_2CO_3} K_2 K_3} + \frac{[H^+]}{\gamma_{HCO_3^-} K_3} + \frac{1}{\gamma_{CO_3^{--}}}$$

C_{TOT} should not change. The pH will be assumed to vary linearly with temperature for reasons given above.

To check our original calculations, use pH = 5.73 and work backwards to get P_{CO₂}

$$P_{CO_2} \frac{(0.13 \times 10^{-3})}{0.0821 (455)} = 0.0034 - \frac{1.06 \times 10^{-11}}{0.175 (0.0201)} \frac{(10^{-5.73})^2}{1.112 \times 9.83 \times 10^{-8} \times 2.73 \times 10^{11}} + \frac{10^{-5.73}}{0.600 \times 2.73 \times 10^{-11}} + \frac{1}{0.121}$$

$$\begin{aligned}
 &= 0.0034 - 3.014 \times 10^{-9} (1.16 \times 10^6 = 1.137 \times 10^5 + 8.2) \\
 &= 0.0034 - 0.00384
 \end{aligned}$$

<0

What happens doing calculator arithmetic is that round-off errors especially on pH are giving meaningless results. The reason stems from the fact that we are dealing with very small differences between two numbers of equal magnitude. Physically the meaning is most of the carbon in the system is in the H_2CO_3 or HCO_3^- forms. Very little exists in the gas phase. (Almost none exists as $\text{CO}_3^{=}$ either).

The conclusion from this exercise is that accurate measurement of gas breakout conditions still requires experimental measurements. Rigorous chemical equilibrium computer codes which can predict effects of temperature and brine chemistry on scaling phenomenon are known to be under development. Their use in geothermal applications is not yet widespread. A serious problem with many of the codes is lack of precise equilibrium data for individual reactions.

Michels (1981) discusses similar problems with equilibrium calculations. He extends his work to flash plants. The article emphasizes the need for good experimental data to supplement any mathematical predictions.

4.0 BRINE COOLING TESTS

A series of brine cooling tests were designed to determine the effect of temperature and transport time on the mass of particles that might be found at the injection well inlet of the Heber Binary Cycle Demonstration Plant. The information is important for determining operating temperatures for the plant outlet brine. Present temperature limits have been set at 150°F at the injection well. Lowering that temperature limit will increase the power output of the plant significantly. Even at 6000 gpm brine flow, a 10°F lowering of the outlet temperature could increase gross power output by 1 megawatt. The potential danger in cooling the brine too much is that particulates might form and plug off the injection wells earlier than planned.

A series of five tests was run to determine increase in solids loading of the brine due to cooling below 150°F. Tests were run at 150, 140, 130, and 120°F. The 120°F case was repeated at two different residence times. In all tests the feed brine was pre-filtered to remove particles >20 microns which were carried up the well. This pre-filtered brine was then cooled and filtered as described later. The rationale for pre-filtering was to avoid trying to measure small differences between large numbers. That is, there was reason to believe the weight of solids coming up the production well at the plant inlet would exceed the weight of solids formed by just cooling the brine in a series of heat exchangers. Hence, the apparatus was designed to process almost solid-free hot brine and then collect any solid materials which formed during some cooling steps.

The original intent of the tests was to look for silica formation only. The tests were intentionally designed to look at worst case conditions; i.e., excess cooling followed by long residence times. If amorphous silica is an important precipitating species, its concentration will depend on transport time because the kinetics of formation are slow (Iler, 1979).

4.1 FILTRATION EQUIPMENT

Figures 4.1 and 4.2 show the isometric and flow diagrams for equipment used in the cooling tests. The system was designed to simulate the Heber plant

FIGURE 4.1. Isometric View of Solids Collection Equipment

FIGURE 4.2. Flow Diagram for Solids Collection Equipment

parameters which were important to silica scaling. The two most important parameters were taken to be temperature and residence time. Deposition of amorphous silica from brines is determined by kinetics and is typically slow unless supersaturation ratios are very high (Iler 1979). Experimentally all the tests were designed to be close to the Heber plant conditions, but also chosen to lean toward maximizing the amount of silica which might form, if it was going to precipitate.

The equipment shown in Figure 4.1 was sized to simulate residence times in the Heber plant and injection line for brine flow rates of 6000 gpm. A brine sample stream (usually close to 600 cc/min) from the plant inlet line was first filtered using a 20 micron brass filter. The pre-filtered brine flowed through about 20 ft of 1/4 in. stainless steel tubing to the apparatus in Figure 4.1. A 100 cc/min side stream was filtered to collect representative material passing through the 20 micron filter. This pre-filtered brine filter was expected to catch a representative sample of the solid material in the brine which was smaller than 20 microns.

The remaining 500 cc/min of brine passed through a concentric tube heat exchanger which cooled the brine to representative plant outlet temperatures. In essence this heat exchanger modeled the actual plant heat exchangers with one exception; the modeled residence times were somewhat shorter than those in the real plant. They were closer to what might be expected at full design brine flows for the plant. It should be noted that if silica solutions are cooled rapidly, the silica is quenched into solution (Barnes, 1976). Silica can then precipitate only very slowly. The Heber plant at flows of 6000 gpm brine will produce some quenching. Another 100 cc/min stream of brine just out of the exchanger was filtered to collect a representative sample of solids which formed because of this quenching.

The remaining 400 cc/min of brine was split into two streams. (Pressure was first reduced to 40 psig to minimize operating problems with the lag vessel.) A 100 cc/min stream flowed into the lag vessel. This lag vessel was sized to give residence times at least as long as those in the actual plant injection line running from plant outlet to the injection well (assuming 6000 gpm brine flow from the plant). Most tests exceeded the actual injection

line residence time in order to produce the most favorable conditions for silica deposition. The walls of the lag vessel were coated with Teflon® to keep solids from building on a metal surface. The intent was to collect all of the solids on the simulated injection well filter at the outlet of the lag vessel. Fluid from this final filter then flowed to a pH probe before being collected in a plastic carboy.

The remaining 300 cc/min stream from the outlet of the heat exchanger ran through a heating coil around the outside of the lag vessel. This heating coil kept the brine temperature at the vessel outlet to within 3°F of the brine temperature at the vessel inlet. The 3°F temperature drop was considered reasonably close to the actual change in the real injection line for the Heber plant. A 50-watt electrical resistance type heater provided backup heating to maintain a constant small temperature gradient in the lag vessel.

For each test, the filtrate from the three filters was collected in carboys and weighed periodically to determine the flow rate of brine through each filter. Some liquid samples were saved for later analyses. All of the filters on the test stand were 49 mm diameter Teflon discs rated to catch 0.45 micron and larger particles.

At the same time as the tests were being run on the test stand, separate sample streams of the plant inlet and outlet brines were filtered through the same style filter and filter papers used on the test stand. The filter on the brine inlet stream was to collect a representative sample of material coming up the injection well. Flows were set so velocities in the sample tubing matched velocities of fluid going to the test stand. Flows through the filter on the actual plant brine outlet line were then adjusted to closely match the velocities on the inlet filter.

4.2 BRINE COOLING TEST RESULTS

The test results are presented in two sections. First the amounts of solids collected in each test are summarized. Second the analytical information is presented to aid in understanding the raw field data.

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4.2.1 Field Data

Each test started by adjusting the set point on the temperature controller and allowing the system to equilibrate overnight. During this equilibration period the filters were in place, but the brine flow by-passed them. Once the system reached its desired operating flows and temperatures, brine flows were directed through the filters.

After each test, filter papers were dried a minimum of three hours at 120°C then weighed to determine the mass of particles collected. Usually five filters were weighed for each test: three from the test stand plus one on the plant inlet line and one on the plant outlet line. Particulate loading for all of the sample streams was determined by collecting and weighing all the filtrate which passed through a given filter while the solids were being collected. One can calculate a particle loading as mg of solids/liter of brine, knowing both the weight of the solid collected and the volume of liquid collected. Total filtering times varied from run to run but fell between 3.8 and 4.7 hours.

Figure 4.3 shows a temperature trace from two separate recorders for Run B. Notice there are actually three temperature traces on the upper portion of the plot. The top of the lag vessel and the middle of the vessel were at identical temperatures for this run. The pH temperature (shown in the bottom half of the figure) was measured downstream of the last filter and next to an in-line pH probe which monitored the brine continuously. For historical records, additional temperatures and the pH value were recorded on a data logger at 15 minute intervals whenever the filters were exposed to brine. The additional temperatures were recorded for the inlet brine to the test stand and for the brine entering the simulated injection well filter. Another thermocouple monitored the temperature of the small heating element in the vessel.

Throughout the test period which lasted six days, the plant ran at very stable conditions. There were no known problems with any of the wells or down-hole pumps. The data should be a good representation of what can be expected under "normal" operating conditions. The plant was operating at only 6000 gpm brine flow. This is considerably below design rates for full capacity. However, for purposes of this test, the reduced rates would give worst case values

FIGURE 4.3. Typical Temperature Traces for the Cooling Tests

for silica deposition due to cooling. This is true because silica formation is a time dependent phenomenon. Other things being equal, more silica should form in the injection lines at 6000 gpm than at full flow, because of longer residence times.

Table 4.1 summarizes the information on amount of solids collected as temperature and time varied. Data is presented chronologically. The important numbers to compare are mg/liter at each point as the temperatures change.

Solids loading at the plant inlet varied from 1.25 mg/liter down to 0.49 mg/liter from the first to the last day of testing. For reference a

TABLE 4.1. Summary of Tests at the Heber Binary Plant Precipitation

Run No.	B	C	D	E	F
Simulated Injection Well Inlet					
Lowest Target Temperature (deg F)	130	120	140	150	120
Date	1-22-86	1-23-86	1-24-86	1-25-86	1-27-86
Actual plant inlet					
Temp (deg F)	360	360	360	360	360
Press (psig)	200	185	195	190	185
mg/liter total solids	1.25	1.22	0.77	0.47	0.49
Actual plant outlet					
temp (deg F)	150	**	150	150	150
Press (psig)	425	**	425	425	425
mg/liter total solids	1.2	**	0.86	0.95	1.07
Pre-filtered hot brine					
Temp (deg F)	296	286	315	305	302
mg/liter solids increase	0.07	0.06	0.04	0.08	0.04
Simulated plant outlet					
Temp (deg F)	131	121	130-160	152	120
press (psig)	28	28	28	28	28
mg/liter solids increase	0.15	??	0.11	0.17	0.16
res time (min)	0.34	0.53	0.31	0.39	0.41
Simulated injection well inlet					
Temp (deg F)	129	119	140-160	149	116
press (psig)	28	28	28	28	28
mg/liter total solids increase	0.22	0.43	0.2	0.15	0.44
res time (min)	116	168	100	83	99

1 mg/liter loading translates to 72 lbs per day of solids coming up the wells if brine flows at 6000 gpm. Since the values are all low, the measured variation is not too surprising.

The mg/liter values for solids in the pre-filtered hot brine are all nearly zero. They represent primarily the amount of material smaller than 20 microns which came up the production well.

The simulated plant outlet filter sampled a slip stream of the prefiltered brine, all of which was quenched to the temperature indicated. This was to approximate the effects of real heat exchangers in the Heber plant. At this filter location there was no significant variation in solids loading with time. The filter paper for Run C developed a pin-hole leak during the test and few solids were collected.

The simulated injection well inlet filter processed another slip-stream of the pre-filtered brine. Temperatures were only 2-3°F cooler than the simulated plant outlet filters. The big difference, however, is the time at temperature for this brine sample. The data indicate that total solids formed does depend on residence time. The amount of solids formed also shows a dependence on temperature at these longer residence times.

The actual plant outlet samples show no significant variation with time over the six day test period. The first day showed the highest value but other numbers did not drop as did the plant inlet values. Since the plant brine flow and plant outlet temperature remained constant for the six days there is no concrete explanation for the variation on the inlet samples. Sampling and filter handling techniques were identical all days.

The conclusion from this testing is that the amount of solids added to the brine just by cooling to 130°F instead of 150°F would be insignificant. Cooling to 120°F would increase the loading somewhat, but the total solids added is less than the "normal" variation in solids loading of the inlet brine. In other words most of the solids entering the injection well will come from the production well even if the brine is cooled to 120°F.

4.2.2 Laboratory Analyses

The filtered samples shown in Figure 4.4 represent all of the samples which were collected and weighed. Only eleven of these were analyzed to determine their chemical composition:

- 5 of the Simulated Injection Well Inlet (Runs B through F)
- 3 of the Simulated Plant Outlet (Runs E, B, F)
- 1 of the Simulated Plant Inlet (Run F)
- 1 of the Actual Plant Outlet (Run B)
- 1 of the Actual Plant Inlet (Run C)

This cross section of samples was deemed sufficient for identifying major chemical species in the solids and detecting any trends with temperature or time. No quantitative chemical analyses were attempted because the most important number relative to injection well plugging is total solids produced. That number was determined from filter weights and reported in the previous section. The chemical components are important from a health and safety standpoint anytime the pipes or exchangers are opened and workers are exposed to the solids. The color of the solids on the simulated plant outlet and simulated injection well gives some clues immediately. The black material could be either FeCO_3 or Fe_3O_4 . The reddish brown is characteristic of AsS (Realgar).

All of the analyzed samples were subjected to three analytical techniques:

- Scanning Electron Microscope (SEM) with a Microprobe
- X-ray Diffraction
- X-ray Fluorescence

The scanning electron microscope provides a view of particle sizes and shapes. Its microprobe gives elemental analyses for small areas down to individual particle sizes. Silicon is easily detected and was originally the species of most interest.

X-ray diffraction identifies compounds from their crystalline structure. Amorphous materials will show no identifiable pattern. The technique is not sensitive to trace amounts of materials in complex crystalline mixtures. It is most useful for identifying major crystalline compounds.

Silica Scaling Potential Test (Collected Solids)

FIGURE 4.4. Solid Samples Collected on 0.45 Micron Filters

X-ray fluorescence gives elemental composition information which complements the electron microprobe data. This technique will detect trace amounts of lead and arsenic in the presence of other highly concentrated species. These analyses were performed after it was discovered that little silica had formed but sulfide species had deposited.

The analytical information for the 11 samples is discussed in the order indicated in Figure 4.5.

<u>Run Number</u>	<u>Actual Plant Inlet</u>	<u>Actual Plant Outlet</u>	<u>Pre-Filtered Plant Inlet</u>	<u>Simulated Plant Outlet</u>	<u>Simulated Injection Well Inlet</u>	<u>Transport Time (min.)</u>
E				152°F	149°F	83
D					140-160°F	100
B		150°F		131°F	129°F	116
C	360°F				119°F	168
F			302°F	120°F	116°F	99

FIGURE 4.5. Key to Solid Samples Selected for Analyses

It is important to remember that all pre-filtered plant inlet, simulated plant outlet and simulated injection well inlet samples represent particles which formed because the brine had cooled. The raw inlet brine to the plant was passed through a 20 micron brass pre-filter before reaching any of these filters. Theoretically particles smaller than 20 micron which were in the brine could have been deposited on these filters. Data presented in the previous section showed that very little material smaller than 20 microns had been carried up the well. Hence the analyses presented here represent mainly material that will form when the brine is cooled but with potential contamination from the well-bore solids. Important exceptions are samples designated 4th and 7th in Figure 4.5. These represent raw brine samples and include all solid sizes coming up the well bore. Sample 4 adds to this any solids generated by cooling.

The brass pre-filter mentioned above unfortunately introduced copper into the system as a contaminant. The copper peaks on some of the traces are not expected based on past experience with this and other geothermal brines.

Run E: 360 -- 149°F (Analyzed Samples 1 and 2)

The first two samples analyzed were from filters maintained at conditions as close to the operating plant as the experimental test unit could simulate. The first sample was collected at 152°F while the second was 3°F cooler. The calculated time for the brine to get between the two filters was 83 minutes.

The scanning electron microscope showed a mass of fine particles in sample 1 (Figure 4.6). The elemental analyses accompanying the photograph are typical of feldspars. Feldspars are the most abundant of all minerals and are widely distributed in igneous, metamorphic and sedimentary rocks. They have the general formula $X(Al, Si)_4O_8$ in which X is Na, K, Ca, or Ba (Hamilton, Woolley and Bishop 1974). Potassic feldspars readily alter to clay minerals such as kaolinite. Kaolinite is a white sometimes greyish solid with chemical formula $Al_2Si_2O_4(OH)_4$. The iron and chromium peaks are believed to be from metal shavings off the test stand. All of the tubing exposed to brine was 304 stainless steel. The sulfur peaks are significant because analyses of other samples confirmed the presence of nickel and lead sulfides. Those compounds are likely present here too.

Simulated Plant Outlet

FIGURE 4.6. SEM and Microprobe Data for Analyzed Sample 1

X-ray diffraction identified only a faint quartz signature. The particles, apparently were small enough to appear amorphous to the instrument.

X-ray fluorescence data (Figure 4.7) identified lead as another major species in the scale. It probably formed as a sulfide.

Information from sample 2 (simulated injection well inlet) is not significantly different from sample 1. The electron microscope (Figure 4.8) isolated one nearly pure quartz particle and X-ray diffraction showed a stronger quartz signal. No general area scans were taken, but sulfides are likely present even though they were not among the three selected particles. (Other analyses discussed below support this speculation.) X-ray Fluorescence (Figure 4.9) again confirms the presence of nickel, lead and iron; all of which were initially assumed to exist as sulfides.

FIGURE 4.7. X-Ray Fluorescence Data for Analyzed Sample 1

Simulated Injection Well Inlet

FIGURE 4.8. SEM and Microprobe Data for Analyzed Sample 2

Run D: 360 → 140°F (Analyzed Sample 3)

Analytical information is presented for this run but will not be discussed in detail. Enough operational problems were encountered during the run to raise questions about the validity of the data. The microprobe data in Figure 4.10 suggest clay minerals are present. X-ray diffraction did identify zinc and iron sulfides in the deposit. Both arsenic and lead show prominently on the x-ray fluorescence scan (Figure 4.11).

Run B: 360 → 130°F (Analyzed Samples 4, 5 and 6)

The actual plant outlet sample (sample 4) was solids collected from brine that passed through four heat exchangers in the plant. Feldspars and clay minerals were evident. In this sample the iron peak in Figure 4.12 appears without chromium since there was no stainless steel in the system. The presence of cadmium and antimony is puzzling because neither element was found

FIGURE 4.9. X-Ray Fluorescence Data for Analyzed Sample 2

Simulated Injection Well Inlet

FIGURE 4.10. SEM and Microprobe Data for Analyzed Sample 3

FIGURE 4.11. X-Ray Fluorescence Data for Analyzed Sample 3

in other samples. Initial speculation said the cadmium came from a thread sealant used at the sample port. When a sample of the sealant was analyzed by X-ray fluorescence, no cadmium was found.

X-ray diffraction positively identified quartz and magnetite (Fe_3O_4) as scale constituents. Thermodynamics predicts the magnetite should form at plant outlet conditions. Quartz would not form in the cooling process but could be carried up from the production wells. Even though quartz is the most stable silica species, it forms only after a series of transformations which occur in geologic time periods (Iler 1979).

X-ray fluorescence also identified the cadmium (Figure 4.13A). Strong cadmium peaks will mask out antimony, so the presence of antimony is not obvious by this technique alone. Once again lead and arsenic appear prominently (Figure 4.13B).

Actual Plant Outlet Run B

FIGURE 4.12. SEM and Microprobe Data for Analyzed Sample 4

FIGURE 4.13A. High Energy X-Ray Fluorescence Data for Sample 4

The simulated plant outlet (sample 5) is characterized in Figure 4.14 and 4.15. The "general area" scan from the electron microprobe is a very typical trace for feldspars. The particle sizes in the photograph indicate material less than 20 microns in diameter was collected. Thus the strong signals could be coming from fines carried up the well. Formation of "fresh" feldspars in the short times of these tests would be highly unlikely. The sulfur peak is significant because of its tie with the X-ray fluorescence data.

X-ray diffraction analyses showed only quartz on an amorphous background.

The X-ray fluorescence data in Figure 4.15 show strong lead peaks. Conspicuous by its apparent absence is arsenic. However, lead and arsenic lines are very close to one another. Hence arsenic could be present but the instrument response is dominated by lead. Portions of the lead, iron and zinc are most likely present as sulfides. Their presence accounts for the sulfide peak on the electron microprobe scans.

FIGURE 4.13B. X-Ray Fluorescence Data for Analyzed Sample 4

Figures 4.16 and 4.17 for the simulated injection well inlet are qualitatively the same as for the simulated plant outlet.

Run C: 360 → 119F (Analyzed Samples 7 and 8)

Sample 7 was solid material collected from the raw brine inlet stream. This brine sample was not pre-filtered by the 20 micron pre-filter mentioned earlier. The electron microprobe signatures are very typical of feldspars and clay minerals. Since the brine is cooled very little coming up the wells, these solids represent material carried up from the formation rather than material formed by any processing steps. The sulfur peak is slightly smaller in this sample than in other samples which have been cooled. This is to be expected since the solubility of most sulfides decreases with decreasing temperature. The silicon peak is significant since it is larger than the

Simulated Plant Outlet

FIGURE 4.14. SEM and Microprobe Data for Analyzed Sample 5

FIGURE 4.15. X-Ray Fluorescence Data for Analyzed Samples

associated aluminum peak. Ordinarily the two elements have about equal peaks heights in "pure" clay minerals.

The excess silica gave a strong quartz signal in the X-ray diffraction analysis. X-ray diffraction also gave positive identification for Fe_3O_4 (magnetite) and chamosite (a clay mineral).

The X-ray fluorescence scans in Figure 4.19 show high iron peaks; presumably from the magnetite. Zinc, arsenic and lead are also present in significant quantities.

Although other plant inlet samples were not analyzed their composition should be very close to this one. Throughout the test period, the plant was running very smoothly with no reported pumping or other well problems.

The simulated injection well sample differed from previous simulated injected well samples. First recall the total amount of solids collected/ml of

Simulated Injection Well Inlet

FIGURE 4.16. SEM and Microprobe Data for Analyzed Sample 6

FIGURE 4.17. X-Ray Fluorescence Data for Analyzed Sample 6

brine had increased significantly. The sulfur peak on the electron microprobe scan (Figure 4.20) also increased in size. In addition to zinc, lead and arsenic, thallium was also detected (Figure 4.21). No thallium had been detected in the other samples which were all collected at higher temperatures.

Run F: 360 → 116°F (Analyzed Samples 9, 10 and 11)

The pre-filtered brine inlet sample was expected to be just a collection of particles which were carried up the well and passed through the 20 micron pre-filter. The electron microscope photo (Figure 4.22) is of interest because the material designated as a "particle agglomerate" is identical in appearance to amorphous silica polymers which have been seen in other geothermal brines. This cluster however was apparently a feldspar contaminated with tubing material from the test stand. The other traces show nothing unusual.

The X-ray diffraction film showed some very strong lines, but the compound(s) could not be identified.

Actual Plant Inlet

"Run C"
Filter at 360 °F

General Area
@ 100 X

"Run C"
360 °F

(1) Individual Particle

"Run C"
360 °F

(2) Individual Particle

FIGURE 4.18. SEM and Microprobe Data for Analyzed Sample 7

FIGURE 4.19. X-Ray Fluorescence Data for Analyzed Sample 7

The final simulated plant outlet sample analyses (Figures 4.24 and 4.25) are fairly similar to others already discussed. The high iron content and relatively low lead values should be compared with those in Figures 4.26 and 4.27.

The difference between the above sample (sample 10) and the simulated injection well inlet sample (sample 11) is the time allowed for the brine species to react before filtering. The simulated injection well sample was only 4°F cooler than the simulated plant outlet sample, but it was collected 99 minutes later. This additional reaction time allowed thallium to precipitate and also increased the amounts of lead and arsenic found in the solid material.

The qualitative chemical analyses and quantitative particulate measurements are summarized in Figure 4.28. The cations shown on each of the samples are listed in approximate order of abundance. Arsenic, lead, and iron were

Simulated Injection Well Inlet

FIGURE 4.20. SEM and Microprobe Data for Analyzed Sample 8

FIGURE 4.21. X-Ray Fluorescence Data for Analyzed Sample 8

always present in much larger amounts than nickel and chromium. Since nickel and chromium were barely detectable in any of the brine samples, the source could be chunks of stainless steel from the sample tubing. (All the copper peaks on the x-ray fluorescent data are attributed to corrosion of the brass pre-filter. Hence Cu is not listed as a potential scale species.)

Shaded areas in Figure 4.28 show relative concentrations (mg/liter) of total solids collected. The base case (100%) was 1.25 mg/l for the actual plant inlet sample for Run B. All other shaded areas represent a fraction of that concentration.

Qualitative Analytical Conclusions:

Formation of amorphous silica from Heber brines cooled even to 120°F is unlikely. None was observed in samples kept at room temperature for 3 months. Other solids (believed to be primarily sulfides) do form in small amounts.

Pre-Filtered Plant Inlet

FIGURE 4.22. SEM and Microprobe Data for Analyzed Sample 9

FIGURE 4.23. X-Ray Fluorescence Data for Analyzed Sample 9

The predominant solid materials coming up the production wells are feldspars and clay minerals. Some quartz will also be found. Magnetite will form (in the absence of H_2S) from iron continuously being added to the brine by corrosion processes. Trace amounts of lead and arsenic also exist probably as sulfides.

As the brine cools, additional solids do form. At a plant outlet temperature of 150°F lead, arsenic and zinc all exist...probably as sulfides. The trend appears to be larger amounts of lead and arsenic compounds forming below 150°C. No really significant difference was observed between 150°F and 130°F. At 120°F, thallium appeared along with the lead and arsenic. The amounts of all three increased significantly with residence time in the test loop.

In an absolute sense the "significant" changes from one run to another are still small in the context of well-plugging problems. Recall a particle loading of 1 mg/liter is about 72 pounds/day of solids entering the wells if the

Simulated Plant Outlet

(1) Particle
Not Shown

FIGURE 4.24. SEM and Microprobe Data for Analyzed Sample 10

FIGURE 4.25A. High Energy X-Ray Fluorescence Data for Sample 10

FIGURE 4.25B. X-Ray Fluorescence Data for Analyzed Sample 10

Simulated Injection Well Inlet

FIGURE 4.26. SEM and Microprobe Data for Analyzed Sample 11

FIGURE 4.27. X-Ray Fluorescence Data for Analyzed Sample 11

brine flow is 6000 gpm. The maximum net increase due to cooling occurred at 120°F and was less than 0.5 mg/liter. Natural variations in particle content of the production wells were greater than any increase in particle content induced by simply cooling the brine.

FIGURE 4.28. Summary of Analytical Data

4.3 THEORETICAL ASPECTS OF COOLING

4.3.1 Silica/Quartz Solubilities

Silica can exist in one of several crystalline states or as an amorphous material (Wahl, 1979; Iler, 1979). Quartz is the abundant naturally occurring form and silica is the form that precipitates from solutions at ordinary temperatures and pressures. Equilibrium between quartz and silica is obtained fairly rapidly at temperatures above 300°F (150°C).

For the reaction:

The quartz solubility is given by: (See Kindle, 1984)

$$\text{Log}_{10} C_0 = 1.93 - 1160/T \quad \text{where } T \text{ is in deg K} \\ C_0 = \text{g/kg H}_2\text{O}$$

In similar fashion the solubility of amorphous silica in pure water is given by

$$\text{Log}_{10} s^0 = -0.1185 - (1.1260 \times 10^3/T) + (2.33 \times 10^5/T^2) \\ + (3.6784 \times 10^7/T^3)$$

where s^0 = molal solubility of amorphous silica in pure water.

T = temperature in degrees Kelvin.

A first order correction for the solubility of silica as it is affected by NaCl in solution is given by:

$$\text{Log}_{10} (s^0/s) = D * m$$

where s = solubility of amorphous silica in salt solution

D = parameter that varies with salt type and temperature

m = molality of the added salt.

Graphical values (Kindle, 1984) for parameter D were fitted to the equation:

$$D = 0.0843 - 0.00022 \cdot T$$

where T = degrees CENTIGRADE

Note: The graphical data were fitted only over a range relevant to the Heber Plant.

Figure 4.29 was generated using the above equations, again only over the range of conditions relevant to the Heber Plant. Assuming a reservoir temperature of 360°F and accepting that quartz equilibrium has occurred in the reservoir, we see from the calculated horizontal line that the ppm SiO_2 is about 245. At plant exit conditions, the form of silica to expect is amorphous. The saturated amorphous silica content at 150°F is 270 ppm. Amorphous silica saturation is calculated to be reached (@ 245 ppm) only if the brine is cooled to 140°F. Elemental silica analyses for the brine have varied between 88 and 110 ppm with the most normal value near 100. This translates to 214 ppm SiO_2 . Using this value we see from the bottom horizontal line that amorphous silica saturation is not reached until the brine is cooled to near 120°F. Effects of pH have been largely ignored in these calculations. Heber brines have a measured pH near 5.3 at plant exit conditions. No chemicals are added or removed by the plant so pH at the well will not be greatly different. Consequently, solubility of silica should not be affected by the slight pH change (due to temperature change) going from plant inlet to the injection well.

The encouraging part of the calculations is they support what was observed in the field; namely, almost no silica formed even when the brine was cooled to 120°F. According to others (Iler, 1979; Owen, 1975), however, the solubility calculations do not always account accurately for observed silica precipitation from geothermal brines. In one case Owen reported an amorphous silica supersaturation of 400% in a highly saline brine with no immediate precipitation of silica. Conversely, no one has reported seeing silica form in a solution where the calculated saturation had not been reached. The important point remains that actual experiments were needed to determine if silica would form in the Heber brine. Calculations say some could have formed at 120°F. Experiments

FIGURE 4.29. Predicted Quartz and Silica Solubilities Relevant to Heber Brine

showed none. At low supersaturations and low temperatures, the kinetics of silica formation is very slow, so seeing no silica in less than two hours at 120°F is not surprising.

4.3.2 Sulfide Solubilities

Some relatively simple equilibrium expressions do exist for predicting the solubility of sulfide minerals in water as a function of temperature and pH. (Czmsnske, 1959; Cobble, 1982). These equations were used to calculate metal ion concentrations in the Heber brine for metals assumed to exist as sulfides. The calculated concentrations were then compared with measured ones. Metal ion supersaturation ratios were taken as indicators of the relative scaling tendencies of four representative sulfides. Lack of data in the required form and limited success of the effort precluded more exhaustive analyses. The calculated values for the lead and zinc ions which would be soluble in solution were more than an order of magnitude lower than the measured analytical values. Other investigators (see Kindle, 1984) have observed poor correlations also and attribute the high analytical values to complexed species usually containing chlorides. Although the supersaturation ratios are not accurate in an absolute sense, they can be used to judge probable trends. For instance, the supersaturation ratio for lead is just over 6 at 360°F, but jumps to 231 at 120°F. This implies we can expect significantly more lead sulfide to form at the 120°F than at 360°F. Experiments verified the implication. For that reason the equations are developed here and some representative results are presented.

The equations below are developed as in Czmsnske, 1959. Equilibrium data were taken from Cobble, 1982 and from Morrey, 1978.

For divalents metal sulfides dissolving in aqueous solutions the following reactions must be considered.

$$\text{M}^{++} + \text{S}^{=} = \text{MS}_{(\text{solid})}\quad K_{\text{SP}} = \frac{1}{[\text{M}^{++}][\text{S}^{=}]} = \text{solubility product for the mineral}$$

Where $\text{H}_2\text{S}(\text{g})$ is in atmospheres and aqueous species []'s are molal activities.

Chemical analysis for total sulfur in solution will give $\text{H}_2\text{S}(\text{aq}) + \text{HS}^- + \text{S}^{=}$.

Thus we can write in terms of concentrations

$$\text{Total Sulfur} = \text{H}_2\text{S}(\text{aq}) + \text{HS}^- + \text{S}^{=}$$

$$\begin{aligned} S_T &= \frac{[\text{H}^+][\text{HS}^-]}{\gamma_{\text{H}_2\text{S}(\text{aq})} K_1} + \frac{[\text{H}^+][\text{S}^{=}]}{\gamma_{\text{HS}^-} K_2} + \frac{K_{\text{SP}}}{\gamma_{\text{S}^{=}} [\text{M}^{++}]} \\ &= \frac{[\text{H}^+][\text{H}^+][\text{S}^{=}]}{\gamma_{\text{H}_2\text{S}(\text{aq})} K_1 K_2} + \frac{[\text{H}^+]}{\gamma_{\text{HS}^-} K_2} \frac{K_{\text{SP}}}{[\text{M}^{++}]} + \frac{K_{\text{SP}}}{\gamma_{\text{S}^{=}} [\text{M}^{++}]} \\ &= \frac{[\text{H}^+][\text{H}^+]}{\gamma_{\text{H}_2\text{S}(\text{aq})} K_1 K_2} \frac{K_{\text{SP}}}{[\text{M}^{++}]} + \frac{[\text{H}^+]}{\gamma_{\text{HS}^-} K_2} \frac{K_{\text{SP}}}{[\text{M}^{++}]} + \frac{K_{\text{SP}}}{\gamma_{\text{S}^{=}} [\text{M}^{++}]} \\ S_T &= \frac{K_{\text{SP}}}{[\text{M}^{++}]} \left\{ \frac{[\text{H}^+]^2}{\gamma_{\text{H}_2\text{S}(\text{aq})} K_1 K_2} + \frac{[\text{H}^+]}{\gamma_{\text{HS}^-} K_2} + \frac{1}{\gamma_{\text{S}^{=}}} \right\} \\ &= \frac{K_{\text{SP}}}{[\text{M}^{++}]} \{X\} \quad \text{where } X = \frac{[\text{H}^+]^2}{\gamma_{\text{H}_2\text{S}(\text{aq})} K_1 K_2} + \frac{[\text{H}^+]}{\gamma_{\text{HS}^-} K_2} + \frac{1}{\gamma_{\text{S}^{=}}} \\ \text{or } [\text{M}^{++}] &= \frac{K_{\text{SP}}}{S_T} \{X\} \end{aligned}$$

First assume that the metal existed only as a sulfide and formed by equilibrating with the metal sulfide in geologic times. Then for a single sulfide mineral we can say

$$M^{++} = S_T$$

$$\text{So } \frac{[M^{++}]}{\gamma_M^{++}} = S_T$$

$$\text{and } [M^{++}]^2 = K_{SP} \gamma_M^{++} \{X\}$$

$$\text{or } [M^{++}] = \sqrt{K_{SP} \gamma_M^{++} \{X\}}$$

Which now gives metal ion activities as a function of temperature and pH.

The equations above will predict activity of metals in equilibrium with their metal sulfides as a function of temperature and pH. To get concentrations from activities of the metal ions one must first calculate activity coefficients as a function of temperature for each ion in solution. Details of the calculation procedure are given in Appendix A. The values shown in Table 4.2 were taken from a series of plots generated from those equations. The plots are unpublished reference materials which are quick to use, but may not generate exactly the same number as the equations because of interpolation errors.

Table 4.3 lists polynomial coefficients for solubility products of the minerals or equilibrium constants for aqueous and gaseous species (Morrey, 1978; Cobble, 1982). The raw solubility data from Cobble were fitted to the

TABLE 4.2. Activity Coefficients for Selected Ions in Heber Brines

	Activity Coefficients for Cations, Determined Manually					
	T = 77F	120F	130F	150F	350F	360F
Fe ⁺⁺	0.292	0.281	0.279	0.27	0.18	0.175
Zn ⁺⁺	0.292	0.281	0.279	0.27	0.18	0.175
Pb ⁺⁺	0.285	0.215	0.205	0.201	0.12	0.121
Ni ⁺⁺	0.292	0.281	0.279	0.27	0.18	0.175
H ₂ S(aq)	1.114	1.113	1.112	1.111	1.112	1.112
HS ⁻	0.355	0.370	0.372	0.376	0.465	0.470
S ⁼	0.26	0.245	0.241	0.238	0.148	0.145

third or fourth order polynomials shown by using least squares regression techniques. The form for the solubility products is:

$$\text{Log}_{10} (K_{\text{Sp}}) = C_0 + C_1 \cdot T + C_2 \cdot T^2 + C_3 \cdot T^3 + C_4 \cdot T^4$$

Where T = deg Centigrade.

The form of the equation is identical for the rest of the reactions except the polynomial equates to $-\text{Log}_{10}(K_{\text{eq}})$.

Table 4.4 shows the calculated equilibrium constants at temperatures relevant to the scaling tests in this study. Table 4.5 gives calculated activities, concentrations, and supersaturation ratios for some selected metals using the ambient in-line pH measurement of 5.3 at 80°F. However, pH is known to

TABLE 4.3. Polynomial Coefficients for Selected Sulfide Equilibrium Reactions

Reaction	C0	C1	C2	C3	C4
$\text{FeS} \rightarrow \text{Fe}^{++} + \text{S}^{--}$	-19.7478	0.0375762	-1.5151216E-04	4.3883781E-07	-5.7741632E-10
$\text{ZnS} \rightarrow \text{Zn}^{++} + \text{S}^{--}$	-27.2281	0.0656348	-2.3736128E-04	6.2287931E-07	-7.5159225E-10
$\text{PbS} \rightarrow \text{Pb}^{++} + \text{S}^{--}$	-30.7752	0.0962129	-3.6419057E-04	9.3929347E-07	-1.1089688E-09
$\text{NiS} \rightarrow \text{Ni}^{++} + \text{S}^{--}$	-11.6770	0.0419803	-1.3286630E-04	2.8854888E-07	-2.8700164E-10
Note: we get pK values below					
$\text{H}_2\text{S}(\text{g}) \rightarrow \text{H}_2\text{S}(\text{aq})$	0.648	0.0172	-1.19700E-04	3.50600E-07	-3.90700E-10
$\text{H}_2\text{S}(\text{aq}) = \text{H}^+ + \text{HS}^-$	7.525	-0.0199	1.16600E-04	-1.32300E-07	
$\text{HS}^- = \text{H}^+ + \text{S}^{--}$	14.69	-0.03361	5.05000E-05	-5.36400E-08	

TABLE 4.4. Solubility Products and Equilibrium Constants of Interest to Scaling Tests

	Temperature in Degrees F					
	77	120	130	150	350	360
$\text{FeS} \rightarrow \text{Fe}^{++} + \text{S}^{--}$	1.27E-19	5.96E-19	8.21E-19	1.50E-18	1.04E-16	1.22E-16
$\text{ZnS} \rightarrow \text{Zn}^{++} + \text{S}^{--}$	1.88E-26	3.03E-25	5.44E-25	1.64E-24	4.59E-21	6.17E-21
$\text{PbS} \rightarrow \text{Pb}^{++} + \text{S}^{--}$	2.61E-29	1.45E-27	3.35E-27	1.63E-26	9.01E-22	1.33E-21
$\text{NiS} \rightarrow \text{Ni}^{++} + \text{S}^{--}$	1.97E-11	1.23E-10	1.81E-10	3.80E-10	8.02E-08	9.78E-08
$\text{H}_2\text{S}(\text{g}) \rightarrow \text{H}_2\text{S}(\text{aq})$	9.81E-02	5.73E-02	5.21E-02	4.44E-02	3.14E-02	3.18E-02
$\text{H}_2\text{S}(\text{aq}) \rightarrow \text{H}^+ + \text{HS}^-$	7.97E-08	1.53E-07	1.71E-07	2.07E-07	1.20E-02	1.07E-07
$\text{HS}^- \rightarrow \text{H}^+ + \text{S}^{--}$	1.32E-14	6.09E-14	9.97E-14	2.05E-13	9.28E-11	1.21E-10

vary with temperature in geothermal brines. Hence, Table 4.6 was generated using the 5.3 value at 77°F and a calculated value of 5.77 at 360°F. (See Section 3.3 of this report.) Other pH values were calculated by linearly interpolating between these two end points. Justification for this interpolation procedure is simplicity only. Theoretical variations are much more complex but the overall accuracy of the solubility calculations did not warrant further refinement of the pH values.

TABLE 4.5. Activities, Concentrations, and Supersaturation Ratios at Analyzed Ambient pH

	<u>77F</u>	<u>120F</u>	<u>130F</u>	<u>150F</u>	<u>350F</u>	<u>360F</u>	
pH	5.3	5.3	5.3	5.3	5.3	5.3	
H ⁺	5.01E-06	5.01E-06	5.01E-06	5.01E-06	5.01E-06	5.01E-06	
Activities in g/Moles/Liter							
Fe ⁺⁺	2.89E-05	1.98E-05	1.83E-05	1.56E-05	6.34E-06	6.26E-06	
Zn ⁺⁺	1.11E-08	1.41E-08	1.49E-08	1.63E-08	4.20E-08	4.45E-08	
Pb ⁺⁺	3.64E-10	8.53E-09	1.00E-09	1.40E-09	1.52E-08	1.72E-08	
Ni ⁺⁺	3.60E-01	2.84E-01	2.72E-01	2.48E-01	1.76E-01	1.77E-01	
Concentrations in mg/liter for Metal Ion							
	<u>77F</u>	<u>120F</u>	<u>130F</u>	<u>150F</u>	<u>350F</u>	<u>360</u>	<u>Measured</u>
Fe ⁺⁺	5.53	3.93	3.60	3.23	1.97	2.0	1.0
Zn ⁺⁺	0.002	0.003	0.003	0.004	0.015	0.017	0.2
Pb ⁺⁺	0.000	0.001	0.001	0.001	0.026	0.029	0.19
Ni ⁺⁺	72000	59000	57000	54000	57000	59000	0.06
Supersaturation Ratios = Analyzed Conc/Calc Conc							
	<u>77</u>	<u>120</u>	<u>130</u>	<u>150</u>	<u>350</u>	<u>360</u>	
Fe ⁺⁺	0.18	0.24	0.27	0.31	0.51	0.50	
Zn ⁺⁺	80.3	60.9	57.4	50.7	13.1	12.0	
Pb ⁺⁺	567	231	186	132	7.2	6.5	
Ni ⁺⁺	8.3E-07	1.0E-6	1.05E-6	1.1E-6	1.05E-6	1.01E-6	

As an example of the calculation procedure we selected lead at 130°F (54.4°C) and pH = 5.3. See Table 4.5 for numerical data.

TABLE 4.6. Activities, Concentrations, and Supersaturation Ratios at pH's Varying with Temperature

	77F	120F	130F	150F	350F	360F
pH	5.3	5.35	5.37	5.39	5.76	5.77
H ⁺	5.01E-06	4.47E-06	4.27E-06	4.07E-06	1.74E-06	1.70E-06

Activities in Moles/Liter

	77F	120F	130F	150F	350F	360F
Fe ⁺⁺	2.89E-05	1.79E-00	1.47E-06	1.01E-06	2.63E-06	2.22E-06
Zn ⁺⁺	1.11E-08	1.26E-08	1.19E-08	1.06E-08	1.74E-08	1.58E-08
Pb ⁺⁺	3.64E-10	7.64E-10	8.04E-10	9.10E-10	6.29E-09	6.09E-09
Ni ⁺⁺	3.60E-01	2.54E-01	2.18E-01	1.61E-01	2.27E-02	6.28E-02

Calculated Concentrations in mg/liter for Metal Ion

	77F	120F	130F	150F	350F	360F	Measured
Fe ⁺⁺	5.62	3.52	2.93	2.10	0.81	0.71	1.0
Zn ⁺⁺	0.002	0.003	0.003	0.003	0.006	0.006	0.2
Pb ⁺⁺	0.000	0.001	0.001	0.001	0.011	0.010	0.19
Ni ⁺⁺	72000	53000	46000	35000	24000	21000	0.06

Supersaturation Ratios = Anal Conc/Calc Conc

	77F	120F	130F	150F	350F	360F
Fe ⁺⁺	0.18	0.28	0.34	0.48	1.23	1.41
Zn ⁺⁺	80	68	71	78	32	34
Pb ⁺⁺	567	258	234	203	17	18
Ni ⁺⁺	8.2E-7	11.3E-7	13.1E-7	17.1E-7	2.5E-7	28E-7

$$K_{SP} = [Pb^{++}][S^{--}]$$

$$\text{LOG}_{10}(K_{SP}) = C_0 + C_1 \cdot T + C_2 \cdot T^2 + C_3 \cdot T^3 + C_4 \cdot T^5$$

$$\begin{aligned} &= -30.7752 + .0962129 \cdot (54.4) - 3.6419 \cdot 10^{-4} (54.4)^2 \\ &\quad + 9.3929 \cdot 10^{-7} (54.4)^3 - 1.10896 \cdot 10^{-9} (54.4)^4 \\ &= -26.47 \end{aligned}$$

$$K_{SP} = \underline{\underline{3.35 \times 10^{-27}}}$$

Similarly

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]_{aq}} = 1.71 \times 10^{-7} \quad K_2 = \frac{[H^+][S^{--}]}{[HS^-]} = 9.97 \times 10^{-14}$$

Then

$$\begin{aligned} P_b^{++} &= K_{PbS} \gamma_{Pb} \left[\frac{[H^+]^2}{\gamma_{H_2S(aq)} K_1 K_2} + \frac{[H^+]}{\gamma_{HS^-} K_2} + \frac{1}{\gamma_{S^{--}}} \right]^{1/2} \\ &= \left[3.35 \times 10^{-27} (.205) \left\{ \frac{(10^{-5.3})^2}{(1.112)(1.71 \times 10^{-7})(9.97 \times 10^{-14})} \right. \right. \\ &\quad \left. \left. + \frac{10^{-5.3}}{.372 (9.97 \times 10^{-14})} + \frac{1}{.241} \right\} \right]^{1/2} \\ &= \underline{\underline{1.00 \times 10^{-9} \text{ g moles/liter}}} \end{aligned}$$

From graphs generated using equations in Appendix A we get

$$\gamma_{Pb^{++}} = 0.205$$

$$\text{So Concentration} = \frac{[\text{Pb}^{++}]}{\gamma_{\text{Pb}^{++}}} = \frac{1.00 \times 10^{-9}}{0.205} = 4.88 \times 10^{-9} \text{ g moles/liter}$$

$$4.88 \times 10^{-9} \text{ g moles/liter} \times 207/\text{g mole} \times 1000 \text{ mg/g} = \underline{\underline{.001 \text{ mg/liter}}} +$$

Finally the "supersaturation ratio"

$$\frac{\text{Analyzed mg/l}}{\text{Calc mg/l}} = \frac{0.19}{.001} = \underline{\underline{190}} +$$

The four representative metals selected in the preceding tables were each chosen for slightly different reasons. All were positively identified as constituents of the filter cakes for most samples.

Iron is known to form sulfides in geothermal brines if hydrogen sulfide is present. Iron also forms Fe_3O_4 and CuFeS_2 in geothermal systems. This violates one of the assumptions of the previous mathematical development...namely that the metal ion exists only in equilibrium with a simple sulfide. Consequently one would expect iron to be undersaturated with respect to just its divalent metal sulfide. All of the calculated supersaturation ratios are less than 1 as expected.

Nickel was identified in many of the samples and was presumed to be a sulfide. The extremely small supersaturation ratios suggest it did not exist as a sulfide at all. Measured concentrations from liquid samples were near the detection limit of the analytical instrument and were very low. Hence the observed solid nickel might just be a contaminant from the sampling equipment which was all stainless steel. Nickel sulfide does not appear in literature discussions of geothermal scale. The calculations here give the plausible reason...nickel sulfide is too soluble.

Lead and zinc sulfide are both known scale species at other geothermal locations (see Kindle, 1984). Both were about the same concentration in the liquid phase. Lead, however, was always the predominant scale species. Calculations show that the lead concentrations at equilibrium do decrease faster than zinc concentrations at Heber pH values. The same trend has also been reported in neutral and saline solutions by Kindle, 1984.

Thus the calculation procedures do give useful trend information which has been supported by experiments. The accuracy of any given number is unknown however. More sophisticated computerized analyses would be required to accurately predict scaling tendencies. Ideally kinetic information would be needed in addition to the thermodynamic data.

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APPENDIX A

CALCULATION OF ACTIVITY COEFFICIENTS

CALCULATION OF ACTIVITY COEFFICIENTS

An extended Debye-Hückel theory activity coefficient is calculated from:

$$\log \gamma = - \frac{Z^2 A I^{1/2}}{1 + DBI^{1/2}} + bI$$

The expressions have the following significances:

γ = activity coefficient

Z = charge of the ion (in proton charge units)

I = ionic strength of solution

$$= \frac{1}{2} \sum_i C_i Z_i^2 \text{ where } C_i \text{ is in moles/kg}$$

b = empirical parameter characteristic of the electrolyte (3.732533×10^{-2})

D = ion size parameter (Angstroms), characteristic of ion

$$A = \frac{(2\pi N)^{1/2} e^3 \rho^{1/2}}{(\ln 10)(1000)^{1/2} (\epsilon k T_k)^{1/2}}$$

e = absolute electronic charge in esu (4.80298×10^{-10})

ϵ = dielectric constant of solvent (H_2O)

ρ = density (g/cm^3)

k = Boltzmann's constant (1.38054×10^{-16} erg $(^\circ K)^{-1}$)

N = Avagadro's number (6.02252×10^{23} mole $^{-1}$)

T_k = Kelvin temperature

$$B = \left(\frac{8\pi N e^2}{1000 \epsilon k T_k} \right)^{1/2}$$

The dielectric constant ϵ and density ρ are, of course, functions of temperature and pressure. The pressure dependence is neglected in this calculation, and the A and B functions are generated by polynomials in the Celsius temperature T :

$$A = \sum_{i=1}^6 A_i T_i^{i-1} \quad B = \sum_{i=1}^6 B_i T_i^{i-1}$$

with

$$\begin{array}{lll} A_1 = 0.4837703 & A_2 = 1.084343 \times 10^{-3} & A_3 = 3.991983 \times 10^{-6} \\ A_4 = 7.768973 \times 10^{-8} & A_5 = -3.476468 \times 10^{-10} & A_6 = 6.446132 \times 10^{-13} \\ B_1 = 3.240799 \times 10^{-1} & B_2 = 1.742177 \times 10^{-4} & B_3 = -1.350873 \times 10^{-7} \\ B_4 = 3.887196 \times 10^{-9} & B_5 = -1.821230 \times 10^{-11} & B_6 = 3.266652 \times 10^{-14} \end{array}$$

NEUTRAL SPECIES - CO₂ TYPE

The activity coefficients for these neutral aqueous are calculated

$$\log \gamma = c_1 + c_2 X + c_3 X^2$$

where X is the molality of the solution. The parameters c_1 , c_2 , and c_3 are functions of temperature calculated from Celsius temperature T using

$$c_1 = \sum_{i=1}^3 e_i T_i^{i-1} \quad c_2 = \sum_{i=1}^3 f_i T_i^{i-1} \quad c_3 = \sum_{i=1}^3 g_i T_i^{i-1}$$

with

$$\begin{array}{lll} e_1 = 9.986931 \times 10^{-1} & e_2 = 7.336486 \times 10^{-5} & e_3 = -3.496592 \times 10^{-7} \\ f_1 = 3.10031 \times 10^{-1} & f_2 = -2.84887 \times 10^{-3} & f_3 = 1.26263 \times 10^{-5} \\ g_1 = 1.567655 \times 10^{-2} & g_2 = 2.815589 \times 10^{-4} & g_3 = -1.747391 \times 10^{-6} \end{array}$$

NEUTRAL SPECIES - O₂ TYPE

For these species the activity coefficient is set to unity. These include H₄SiO₄, NH₃, O₂, and H₂.

WATER

The water activity coefficient's leading term is such that water activity is near unity. Specifically, water activity coefficient is calculated from

$$\log \gamma = -\log C_{H_2O} - 1.562 \times 10^{-2} I \left(1 - \frac{2.323A}{C_1^3 I}\right) (G - 2 \log G - G^{-1}) \\ + T_2 I + T_3 I^2$$

where

C_{H_2O} = number of moles of liquid water per kilogram of brine

I = ionic strength

$$G = 1 + T_1 a I^{1/2}$$

$$A = \sum_{i=1}^6 A_i T^{i-1} \text{ (previously defined)}$$

$$C_1 = \sum_{i=1}^3 e_i T^{i-1} \text{ (previously defined)}$$

$$T_1 = 1.5$$

$$T_2 = 6.78376 - 357.476/T_k - 0.975765 \ln T_k$$

$$T_3 = -0.657028 + 38.5245/T_k + 0.093631 \ln T_k$$

To determine the activity coefficient type for a given species first look at the species-diameter-charge values in Table A.1. For neutral aqueous species, the charge is zero. Diameter is irrelevant for that case. For charged aqueous species, find in the table the correct absolute value of ion charge and closest ion diameter. Calculate activity coefficient from the above equations using

that diameter and ion charge. Note that the neutral species uses total ionic molality rather than ionic strength as one of the variables.

The unphysical value of 10 for aqueous species charge indicates the species is neutral and an activity coefficient of unity is used. (Type 3 above or O_2 type). Charge zero and non-zero diameter indicates neutral species for which the CO_2 type activity coefficient is used.

TABLE A.1. Relative Diameter and Charge Values for Ionic Species

<u>Ion</u>	<u>Diameter</u>	<u>Charge</u>	<u>Ion</u>	<u>Diameter</u>	<u>Charge</u>
Al ⁺⁺⁺	9	3	K ⁺	3	1
Na ⁺	4	1	Ca ⁺⁺	6	2
Mg ⁺⁺	8	2	Fe ⁺⁺	6	2
Mn ⁺⁺	6	2	Ag ⁺⁺	2	1
Au ⁺	2	1	Pb ⁺⁺	4	2
Zn ⁺⁺	6	2	Cu ⁺	2	1
2Hg ⁺⁺	5	2	H ₄ SiO ₄	0	10
As(OH) ₄ ⁻	4	-1	S ⁺⁺	5	-2
SO ₄ ⁻⁻	4	-2	CO ₃ ⁻⁻	4	-2
Cl ⁻	3	-1	OH ⁻	3	-1
H ⁺	9	1	H ₂ O	0	0
F ⁻	5	-1	NH ₃	0	10
BO ₃ ⁻⁻⁻	5	-3	Ba ⁺⁺	6	2
Sr ⁺⁺	6	2	SbO ⁺	4	1
Cr ⁺⁺	6	2	Ni ⁺⁺	6	2
Al(OH) ⁺⁺	6	2	Al(OH) ₂ ⁺	5	1
Al(OH) ₄ ⁻	4	-1	Al(SO ₄) ⁺	1	1
Al(SO ₄) ₂ ⁻	4	-1	AlF ⁺⁺	4	2
AlF ₂ ⁺	4	1	AlF ₃	4	0
AlF ₄ ⁻	4	-1	AlF ₅ ⁻⁻	4	-2
KCl	4	0	KCO ₃ ⁻	3	-1
KSO ₄ ⁻	3	-1	BaOH ⁺	4	1
NaCl	4	0	NaCO ₃ ⁻	4	-1
NaSO ₄ ⁻	4	-1	SrOH ⁺	4	1
CaOH ⁺	4	1	CaCO ₃	4	0
CaHCO ₃ ⁺	5	1	CaSO ₄	4	0
MgOH ⁺	4	1	MgCO ₃	4	0
MgHCO ₃ ⁺	4	1	MgSO ₄	6	0
MgF ⁺	4	1	Fe(OH) ⁺	4	1
Fe(OH) ₂	4	0	FeCl ⁺	4	1
FeCl ₂	4	0	FeCl ₃ ⁻	4	-1

TABLE A.1. (contd)

Ion	Diameter	Charge	Ion	Diameter	Charge
CrCl^{++}	5	2	CrCl_2^+	4	1
FeSO_4	4	0	Fe^{++}	9	3
Fe(OH)^{++}	4	2	Fe(OH)_2^+	4	1
Fe(OH)_3	4	0	Fe(OH)_4^-	4	-1
FeCl^{++}	4	2	FeCl_2^+	4	1
FeCl_3	4	0	FeCl_4^-	4	-1
FeSO_4^+	4	1	$\text{Fe(SO}_4)_2^-$	4	-1
FeF^{++}	4	2	FeF_2^+	4	1
FeF_3	4	0	FeF_4^-	4	-1
FeF_5^{--}	4	-2	MnCl^+	4	1
MnCl_2	4	0	MnCO_3	4	0
MnHCO_3^+	4	1	MnSO_4	4	0
Mn^{+++}	9	3	MnCl^{++}	4	2
MnCl_2^+	4	1	MnCl_3	4	0
MnO_4^-	4	-1	AgCl	4	0
AgCl_2^-	4	-1	AgCl_3^{--}	4	-2
AgCl_4^{--}	4	-3	AgSO_4^-	4	-1
NiOH^+	4	1	AgNH_3^+	4	1
$\text{Ag(NH}_3)_2^+$	4	1	AuCl_2^-	4	-1
$\text{Au(NH}_3)_2^+$	4	1	Au^{+++}	9	3
AuCl_4^-	4	-1	$\text{Au(NH}_3)_4^{+++}$	9	3
CuCl	4	0	CuCl_2^-	4	-1
CuCl_3^{--}	4	-2	CuNH_3^+	4	1
$\text{Cu(NH}_3)_2^+$	4	1	HSO_4^-	4	-1
HS^-	3	-1	H_2S	4	0
HCO_3^-	4	-1	H_2CO_3	4	0
HCl	4	0	HF	4	0
Pb(OH)^+	4	1	Pb(OH)_2	4	0
PbCl^+	4	1	PbCl_2	4	0
PbCl_3^-	4	-1	PbCl_4^{--}	4	-2

TABLE A.1. (contd)

Ion	Diameter	Charge	Ion	Diameter	Charge
PbSO ₄	4	0	Pb(SO ₄) ₂ ⁻⁻	4	-2
ZnOH ⁺	4	1	Zn(OH) ₃ ⁻⁻	4	-1
Zn(OH) ₄ ⁻⁻	4	-2	ZnCl ⁺	4	1
ZnCl ₂	4	0	ZnCl ₃ ⁻	4	-1
ZnCl ₄ ⁻⁻	4	-2	ZnSO ₄	4	0
Zn(NH ₃) ⁺⁺	4	2	Zn(NH ₃) ₂ ⁺⁺	4	2
Zn(NH ₃) ₃ ⁺⁺	4	2	Zn(NH ₃) ₄ ⁺⁺	4	2
ZnF ⁺	4	1	NiSO ₄	4	0
Cu ⁺⁺	6	2	CuOH ⁺	4	1
CuCl ⁺	4	1	CuI ₂	4	0
CuCl ₃ ⁻	4	-1	CuCl ₄ ⁻⁻	4	-2
CuSO ₄	4	0	CuNH ₃ ⁺⁺	4	2
Cu(NH ₃) ₂ ⁺⁺	4	2	Cu(NH ₃) ₃ ⁺⁺	4	2
Cu(NH ₃) ₄ ⁺⁺	4	2	CuF ⁺	4	1
HG ₂ SO ₄	4	0	HG ⁺⁺	5	2
HGCl ⁺	4	1	HGCl ₂	4	0
HGCl ₃ ⁻	4	-1	HGCl ₄ ⁻⁻	4	-2
HGSO ₄	4	0	HGNH ₃ ⁺⁺	4	2
HG(NH ₃) ₂ ⁺⁺	4	2	HG(NH ₃) ₃ ⁺⁺	4	2
HG(NH ₃) ₄ ⁺⁺	5	2	HGF ⁺	4	1
H ₃ SiO ₄ ⁻	4	-1	H ₂ SiO ₄ ⁻⁻	4	-2
As(OH) ₃	4	0	HAs(OH) ₄	4	0
As(OH) ₈ ⁻⁻⁻	6	-3	HAs(OH) ₈ ⁻⁻	5	-2
H ₂ As(OH) ₈ ⁻	4	-1	H ₃ As(OH) ₈	4	0
NH ₄ ⁺	4	1	NH ₄ Cl	4	0
NH ₄ SO ₄ ⁻	4	-1	H ₈ O ₃ ⁻⁻	5	-2
H ₂ BO ₃ ⁻	4	-1	H ₃ BO ₃	4	0
BaCO ₃	4	0	BaHCO ₃ ⁺	4	1
BaSO ₄	4	0	SrCO ₃	4	0
SrHCO ₃ ⁺	4	1	SrSO ₄	4	0

TABLE A.1. (contd)

<u>Ion</u>	<u>Diameter</u>	<u>Charge</u>	<u>Ion</u>	<u>Diameter</u>	<u>Charge</u>
Cr^{+++}	9	3	O_2	0	10
Ni^{+++}	9	3	H_2	0	10
HSbO_2	4	0	SbO_2^-	4	-1
SbCl_4^-	4	-1	SbO_3^-	4	-1
SbCl_6^-	4	-1	Undefined	0	0
CrF^{++}	5	2	CrF_2^+	4	1
CrF_3	5	0	NiNH_3^{++}	5	2
$\text{Ni}(\text{NH}_3)_2^{++}$	5	2	$\text{Ni}(\text{NH}_3)_3^{++}$	5	2
$\text{Ni}(\text{NH}_4)_4^{++}$	5	2	$\text{Ni}(\text{NH}_4)_5^{++}$	5	2

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