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**THE USE OF GEOCHEMICAL-EQUILIBRIUM COMPUTER
CALCULATIONS TO ESTIMATE PRECIPITATION
FROM GEOTHERMAL BRINES**

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THE USE OF GEOCHEMICAL-EQUILIBRIUM COMPUTER CALCULATIONS TO ESTIMATE PRECIPITATION FROM GEOTHERMAL BRINES

Abstract

We have used the Helgeson-Herrick geochemical code to calculate the solubility of NaCl, KCl, and KCl-NaCl in water and to predict which minerals will precipitate from Salton Sea Geothermal Field brines. The code's predictions of sulfide-silicate precipitation from the Magmamax #1 brine are in good agreement with field tests of scaling, although the observed sulfide-silicate scale matrix is in amorphous form, rather than the cry-

stalline form predicted by the code. The code's predictions of scale precipitation from wells with different brine compositions are also in good agreement with field tests. The code appears to be a useful screening tool, despite reservations about the use of purely thermodynamic predictions in systems with important kinetic constraints. We have suggested several ways to improve and apply the code in the future.

I. Introduction

A major goal of the LLL geothermal project is to develop a total flow concept for converting the thermal energy of high-temperature, high-salinity brines — found in the Salton Sea Geothermal Field (SSGF) — to electric power. LLL's approach to the total flow process calls for passing the entire wellhead product through stationary, specially designed nozzles to form high-velocity jets. These jets then turn an axial-flow impulse turbine that generates electricity (Austin et al., 1973). Unfortunately, as the high-salinity brines

cool and flash (i.e., are made to do work) large quantities of sulfides and silicates precipitate, producing a ubiquitous scale on pipes, nozzles, and turbine blades (Owen and Jackson, 1976). Figure 1 shows the nature and composition of the scale deposited on an expansion nozzle (Owen, private communication, 1976).

Numerous ways to control scale have been suggested. Changing the oxidation state, for example, may reduce or eliminate some of the precipitating constituents (Jackson and Owen,

Fig. 1. Mineral components of scale precipitating on an expansion nozzle. The flow of Magmamax #1 brine is indicated. After L. Owen, private communication, 1976.

1975). Preliminary field tests indicate that lowering the pH may also be a successful method (Grens and Owen, 1976).

The brines are complicated by both the large number of species present and by the complexity of the chemical reactions occurring. Table 1 presents representative analyses of brines from the Sinclair #4 and Magmamax #1 wells. The brine solutions are very concentrated (5 molal, ionic strength 6), containing mostly NaCl. There are also significant amounts of Ca^{+2} , K^{+} , as well as H_4SiO_4 , Fe^{+2} , Cu^{+2} , Pb^{+2} , Mn^{+2} , Mg^{+2} , S^{-2} , CO_2 , and H_2S . As a result of widespread chloride and hydroxyl complexing in these reducing brines (as evidenced by S^{-2} and Fe^{+2}),

there are many interdependent and complicated equilibria. Clearly, the precipitation of silica and metal sulfide scale is of special interest because of the scale's corrosive effect on plant materials and its unbalancing effect on the turbine.

Precipitation equilibria can be studied by thermodynamic equilibrium calculations (both those done by hand and by computer code) and by experiment. Hand calculations, however, are either tedious or impossible in multicomponent systems. Laboratory or field experiments on SSGF brines are costly, time-consuming, and hard to perform.

Because of these deficiencies in experimental methods of examining

Table 1. Brine composition of wells in the Salton Sea Geothermal Field.

Species	Sinclair # 4 Reservoir fluid composition			Magmamax # 1 Reservoir fluid composition		
	ppm	Mols/ kg fluid	Mols/ kg water	ppm	Mols/ kg fluid	Mols/ kg water
Al	2.000×10^0	7.412×10^{-5}	9.515×10^{-5}	1.593×10^2	5.904×10^{-3}	7.510×10^{-3}
Ba				7.017×10^2	5.109×10^{-3}	6.499×10^{-3}
B				3.358×10^2	3.106×10^{-2}	3.951×10^{-2}
Ca	2.250×10^4	5.614×10^{-1}	7.206×10^{-1}	1.982×10^4	4.945×10^{-1}	6.290×10^{-1}
Cl	1.300×10^5	3.667×10^0	4.707×10^0	1.049×10^5	2.959×10^0	3.764×10^0
CO ₂	4.000×10^3	9.089×10^{-2}	1.167×10^{-1}	2.583×10^4	5.869×10^{-1}	7.465×10^{-1}
Cu	3.000×10^0	4.721×10^{-5}	6.061×10^{-5}	1.205×10^0	1.896×10^{-5}	2.412×10^{-5}
F				1.722×10^2	9.064×10^{-3}	1.153×10^{-2}
Fe	1.150×10^3	2.059×10^{-2}	2.643×10^{-2}	2.411×10^2	4.317×10^{-3}	5.491×10^{-3}
Pb	7.800×10^{-1}	3.765×10^{-4}	4.833×10^{-4}	3.444×10^1	1.662×10^{-4}	2.114×10^{-4}
Li				1.468×10^2	2.116×10^{-2}	2.691×10^{-2}
Mg	5.900×10^1	2.427×10^{-3}	3.115×10^{-3}	9.643×10^1	3.966×10^{-3}	5.045×10^{-3}
Mn	9.500×10^2	1.729×10^{-2}	2.220×10^{-2}	6.578×10^2	1.197×10^{-2}	1.523×10^{-2}
K	1.160×10^4	2.967×10^{-1}	3.808×10^{-1}	9.480×10^3	2.424×10^{-1}	3.084×10^{-1}
SiO ₂	4.213×10^2	7.012×10^{-3}	9.001×10^{-3}	5.123×10^2	8.526×10^{-3}	1.085×10^{-2}
Ag	5.000×10^{-1}	4.635×10^{-6}	5.950×10^{-6}	4.305×10^{-1}	3.991×10^{-6}	5.076×10^{-6}
Na	5.070×10^4	2.205×10^0	2.831×10^0	4.999×10^4	2.174×10^0	2.766×10^0
Sr				4.589×10^2	5.237×10^{-3}	6.662×10^{-3}
S	6.000×10^0	1.871×10^{-4}	2.402×10^{-4}	3.248×10^1	1.013×10^{-3}	1.288×10^{-3}
Zn				2.428×10^2	3.714×10^{-3}	4.724×10^{-3}
Total Dissolved Solids	2.170×10^5			1.880×10^5		
pH	4.500×10^0			6.500×10^0		

brines, the Laboratory has also employed geochemical-equilibrium codes, which can model numerous simultaneous reactions. Geochemical code models permit rapid and relatively cheap parameter studies of the effects of additives, pH changes, and oxidation on mineral precipitation from the brine.

They can thus serve as a screening mechanism to minimize costly experiments, avoid tedious hand calculations, and account for differences between various wells or changes in any given well as a function of time. Geochemical codes may also be used to model reinjection equilibria as a

function of pH and temperature and to study corrosion problems in hypersaline environments.

A large geochemical code is absolutely necessary to treat complex, dirty natural systems such as SSGF brines. To some extent, the Helgeson-Herrick is such a code because it examines pH and oxidation state changes as a function of temperature. We have used the code in this work and it will be described in more detail in Section II.

Note, however, that predictions based solely on thermodynamic grounds are limited. For example, simply because minerals are predicted to precipitate does not necessarily mean that they will. Kinetics may inhibit precipitation. Moreover, the formation of scale also depends on crystallization, adherence, and hydrodynamics (Vetter, private communication, 1976), as well as kinetic considerations. These influences are not part of the thermodynamic data base and must be studied in the laboratory or in the field. As a result, the valid application of geochemical equilibrium codes necessitates constant interaction between codes and field or laboratory experiments. For example, the HH code has predicted that quartz precipitates under certain conditions at all pH's between 2 and 10. However, it is already known that coagulation of silica is inhibited at

lower pH's (Iler, 1955). Consequently, kinetic considerations indicate that silica may not precipitate rapidly enough to form scale. In this case, interacting code with experiment allowed us to consider the effect of kinetics on the formation of scale. On occasion, such interactions could also lead to the discovery of substances totally omitted from the thermodynamic data base. We shall now examine these points more systematically.

If thermodynamics predicts that a mineral or a mineral assemblage will not appear, then that mineral or mineral assemblage cannot appear. Consequently, its appearance experimentally or in scale indicates that either a specific mineral or mineral assemblage is not in the code's data base or else the thermodynamic input data for these minerals needs revision. In either case, the code's data base needs reconsideration. It is also possible that a mineral or mineral assemblage (e.g., iron-silica) will either appear in amorphous form — rather than as identifiable crystals — or will coprecipitate.

If thermodynamics predicts that a mineral or a mineral assemblage will appear, then it may or may not appear. It may not appear in the scale, but it may be suspended in the brine (e.g., because of nonadherence). If it does not appear at all, then the kinetics of precipitation is slow

with respect to the time-scale of the experiment. This latter situation can be easily handled by eliminating the mineral or suite of minerals from subsequent calculations for this system.

The above considerations illustrate that the geochemical code's data base, which includes activity coefficient approximations, is an important component of successful calculations. Equally important is the interaction with experiment. Once reasonable consistency is achieved between code predictions and experiment under known conditions, then the code can be used for a wide range of parameter studies of pH, oxidation state, temperature, etc.

All these caveats may appear discouraging. However, our results, described in Section III, are consistent with LLL field experiments, including differences between wells.

In fact, our calculations illustrate qualitatively the changes that should result from altering both the pH and oxidation state of the brine. In agreement with chemical intuition, quartz disappears at high pH, but large quantities of undesirable silicates precipitate. Less intuitive, however, is the fact that highly oxidized brines precipitate Fe oxides at all pH's and may even yield anhydrite.

In this paper, we

- Describe the geochemical code used in our calculations
- Use the code to
 - Check the solubility for the test systems NaCl, KCl, and KCl-NaCl in water
 - Calculate which minerals will precipitate from oxidizing and reducing brines
- Outline future applications of the code

II. Description of the Helgeson-Herrick Code

The Helgeson-Herrick code is a geochemical equilibrium code specifically designed to find the equilibrium points resulting from the step by step dissolution of a mineral assemblage in water or in a relatively dilute solution of electrolytes. It

consists of

- A large, complicated iteration routine for locating the equilibrium point of each step
- A set of activity coefficient (γ) approximations for all ionic species

- A data base of the prerequisite equilibrium constants and solubility products

The code calculates the equilibrium species and minerals present at each step in a series. During each step, a small amount of rock is added to a solution. The series of steps proceed until the solubilities of all the mineral constituents of the rock are reached. Along the way, new phases may appear or even subsequently disappear before the final equilibrium is reached. The code allows the constituent rock minerals to be added to the solution at different relative rates.

The original Helgeson code (Helgeson, 1968; Helgeson et al., 1969; 1970) found the equilibrium of each step essentially by expanding the nonlinear expressions for equilibrium constants and solubility products into a second-order Taylor series. The result, which was in matrix form, was solved iteratively for corrections to the initial estimates of concentrations by matrix inversion. This method of solution involves all possible species and thus effectively involves the inversion of large matrices.

The original code created an effective mechanism for investigating large, complex, aqueous geochemical systems. However, because of its academic origins, it was not possible

to optimize it for speed and efficiency; hence, it was slow and cumbersome. During the past few years, Dr. Claude Herrick of Los Alamos Scientific Laboratory has upgraded the numerical analysis portion of the code and replaced the Taylor series technique with a more efficient predictor-corrector method. These recent changes have increased the code's speed, but they have not altered the code's fundamental design. We have used the Helgeson-Herrick version, kindly provided by Dr. C. Herrick, in all of our calculations.

There are several reservations to the use of the HH code. First, the code's data base consists of over 100 mineral and over 100 aqueous species (Helgeson, 1967; 1968; 1969). The data base we used is about 6 years old and most certainly possesses errors and missing species. Recently, Zen (1972) has pointed out inconsistencies in Gibbs energy, enthalpy, and entropy of minerals such as corundum, kaolinite, muscovite, paragonite, pyrophyllite, zoisite, kyanite, andalusite, and sillimanite and has stated that the "validity of all thermochemical calculations for mineralogical phase reactions involving aluminum is suspect." Second, the activity coefficient approximations are valid only for dilute solutions, whereas we are concerned with concentrated brines (see Table 1).

There is a third reservation. The fundamental purpose of the code is to calculate the results of dissolving a rock in water or in a dilute electrolyte solution. It is not designed for our case, in which a concentrated, saturated brine is flashed or cooled, thereby precipitating a host of silicates and sulfides. In such circumstances, the HH code does not converge; it simply crashes. Fortunately, the code yields the mineral assemblage that precipitates from the hypersaline brine; i.e., what is expected thermodynamically to appear

in the scale. Unfortunately, it does not report amounts of precipitates or concentrations of the aqueous species.

Despite these difficulties, we do get an idea of the suite of minerals expected to precipitate. Moreover, the predictions are in reasonable agreement with field observations. Consequently, the results from the HH code have been of value to the LLL Geothermal Program. In Section III, we describe the results of several hundred runs, many of which were made to debug the program and get the code operating.

III. Results

We have used the Helgeson-Herrick code to investigate the solubility relations in the following systems: NaCl-H₂O, KCl-H₂O, NaCl-KCl-H₂O, Sinclair #4 brine, and Magmax #1 brine. We shall present results of this investigation in the order listed.

A. NaCl-H₂O

We have investigated the solubility of NaCl (halite) in water as a function of the following temperatures: 25°, 100°, 150°, 200°, 250°, and 300°C (Fig. 2). We were unable to determine solubilities at other temperatures because the code is

only operational at the specified temperatures listed above.

It is apparent that there is

- Good agreement between the two experiments at temperatures below 275°C
- Poor agreement between the code results and experimentally determined solubilities at all temperatures

Some of the reasons for this disparity have been pointed out in the introduction. In particular, we believe that the activity coefficient approximations are the major cause of lack of agreement. As noted earlier, these

Fig. 2. Solubility of NaCl in H₂O as a function of temperature.

approximations were designed for dilute rather than saturated salt solutions.

B. KCl-H₂O

We have investigated the solubility of KCl (sylvite) in water as a function of the following temperatures: 25°, 100°, 150°, 200°, 250° and 300°C (Fig.

3). As noted above, data at intermediate temperatures cannot be obtained. Once again, there is poor agreement between the experimentally determined solubility data of Shearman and Menzies (1937) and the results of the code at all temperatures. Again, we believe the activity coefficient approximations are primarily responsible for this lack of agreement.

Fig. 3. Solubility of KCl in H₂O as a function of temperature.

C. NaCl-KCl-H₂O

We have investigated the solubility of KCl-NaCl mixtures in water as a function of the following temperatures: 25°, 100°, 150°, 200°, 250°, and 300°C. Results for 25°, 100°, and 200°C are shown in Figs. 4, 5, and 6, respectively.

Data at 25°C (Fig. 4) indicate that there is poor agreement between code results and the experiments reported by Seidell (1953). At low KCl concentrations, the code solubilities of NaCl are systematically higher than experiment. At high KCl concentrations, the predicted code

Fig. 4. Solubility of KCl and NaCl in H₂O at 25°C.

solubilities of NaCl are generally lower than determined experimentally. However, the lack of agreement is reminiscent of the lack of agreement for NaCl-H₂O and KCl-H₂O.

The same relationship between code and experiment obtains in Fig. 5. The predicted code solubilities of NaCl at low KCl concentrations are higher than the experimental data of Cornec

Fig. 5. Solubility of KCl and NaCl in H₂O at 100°C.

and Krombach (1932), and just the opposite at high KCl concentrations. One interesting feature revealed at the 100°C isotherm is the poor agreement even between the experimental data of Cornec and Krombach (1932) and Acknow and Wassilijew (1932). However, the one essential point

depicted in Fig. 5 is the poor agreement between the predicted code solubilities and the experimental data of both investigations.

Fig. 6 shows that the greatest discrepancy is between the HH code results and the experimental data of Akhumov and Vasil'ev (1932). At

Fig. 6. Solubility of KCl and NaCl in H₂O at 200°C.

this temperature, the code-predicted NaCl solubilities are much lower than the experimental results at all KCl concentrations, with the greatest deviations occurring at high KCl concentrations. Again, the lack of agreement in these mixed concentrated solutions is most probably due to inadequate dilute solution activity coefficient approximations.

Note, however, that despite the relatively poor agreement, the predicted curves do show the same trends as the experimental points at all temperatures.

D. Sinclair #4 Brine

We have used the HH code to survey the effects of changing the pH and oxidation state, using the analysis of brine from the Sinclair #4 well as input (Table 1). We have studied the minerals which precipitate from this brine as a function of pH and temperature (60°, 100°, 150°, 200°, and 250°C) under reducing and oxidizing conditions, where these are meant to be boundary conditions; i.e., very oxidizing and very reducing (Table 2).

Figures 7 through 11 display the results of the survey. The numbers on the figures refer to compounds shown in Appendix B. Note, however, that sulfides have been specified by formula because they are significant

Table 2. Brine conditions.

	Oxidizing	Reducing
SO_4^{-2}	$2.4 \times 10^{-4} \text{ m}$	$1 \times 10^{-30} \text{ m}$
S^{-2}	$1 \times 10^{-30} \text{ m}$	$2.4 \times 10^{-4} \text{ m}$

constituents of the scale (Quong, 1976), are few in number, have simple formulas, and are best predicted by the code.

Several features are worthy of comment. For an oxidizing brine between 60° and 250°C (Table 2) no sulfides precipitate throughout the entire range of pH studied, but a host of silicates and oxides can crystallize. Iron-rich phases such as haematite, magnetite, ferric hydroxide, minnesotaite, and greenalite are among the early precipitates predicted in the pH range 2.0 through 4.0. Under reducing conditions, however, the HH code predicts that sulfides and silicates can precipitate as a function of pH and temperature. The sulfide assemblages for a reducing brine are shown in Table 3. The code predicts that sulfide precipitation can be completely suppressed at pH's lower than 3.5 at 150°, 200°, and 250°C, and at pH's lower than 3.0 at 100°C. Native copper was predicted to precipitate from the Sinclair #4 brine under reducing conditions (Fig. 12).

Fig. 7. Precipitation from the Sinclair #4 brine as a function of pH, oxidation state, and temperature (60°C). (See Appendix B for meaning of numbers.)

E. Magmamax #1 brine

We have also used the HH code to survey the effects of altering the pH and oxidation state, using the analysis of brine from the San Diego Gas & Electric Magmamax #1 well as input (Table 1). We have studied the minerals which precipitate from this brine as a function of pH and temperature (60°, 100°, 150°, 200°, and

250°C) under reducing and oxidizing conditions, where these are again meant to be boundary conditions (Table 2) (Figs. 13-17). For an oxidizing brine, between 60° and 250°C a raft of silicates and oxides are predicted to precipitate throughout the entire range of pH studied. Iron-rich phases such as haematite, magnetite, and minnesotaite are

Table 3. Sulfide assemblage at various temperatures (Sinclair #4 brine — reducing conditions).

Temperature, °C				
60°	100°	150°	200°	250°
chalcocite (2) ^a	chalcocite (3)	pyrrhotite (3.5)	pyrrhotite (3.5)	pyrrhotite (3.5)
chalcocite (2)	bornite (3)	chalcocite (4)	galena (4.5)	galena (5)
bornite (2)	pyrrhotite (3.5)	galena (4)	chalcocite (5)	chalcocite (5.5)
galena (2.5)	galena (3.5)		pyrite (6)	
pyrite (2.5)	chalcocite (3.5)	pyrite (5)	bornite (8)	
pyrrhotite (2.5)	pyrite (3.5)	chalcocite (5.5)	chalcocite (10)	

^aThe numbers in parentheses denote the pH of the brine when that particular mineral first appeared (pH is increasing).

Fig. 8. Precipitation from the Sinclair #4 brine as a function of pH, oxidation state, and temperature (100°C). (See Appendix B for meaning of numbers.)

Fig. 9. Precipitation from the Sinclair #4 brine as a function of pH, oxidation state, and temperature (150°C). (See Appendix B for meaning of numbers.)

always among the earliest precipitates predicted under oxidizing conditions.

For a reducing brine, the HH code predicts that a host of sulfides can coprecipitate with a cortège of silicates, oxides, and native metals as a function of pH and temperature. Table 4 shows the sulfide assemblages for a reducing brine. Sulfide precipitation can be completely suppressed

at pH's lower than 3.5 at 150°, 200°, and 250°C, 3.0 at 100°C, and 2.5 at 60°C. Both native copper and silver were predicted to precipitate from Magmamax #1 brine under reducing conditions. Figure 18 illustrates the mode of precipitation of copper and silver as a function of temperature and pH. It is clear that native silver precipitates at lower pH's

Fig. 10. Precipitation from the Sinclair #4 brine as a function of pH, oxidation state, and temperature (200°C). (See Appendix B for meaning of numbers.)

than copper at temperatures less than 150°C.

F. Conclusions

We have used the HH code to investigate solubility relations in the following systems: NaCl-H₂O, NaCl-KCl-H₂O, Sinclair #4, and Magmamax #1 brines. Calculated solubilities

in the simple salt systems generally show poor agreement when compared to the experimental results. However, the similarity between the trends of the calculated solubilities and the experimental points does allow the use of code calculations to provide a general survey of the effects of pH and oxidation state. Thus, we can

Fig. 11. Precipitation from the Sinclair #4 brine as a function of pH, oxidation state, and temperature (250°C). (See Appendix B for meaning of numbers.)

expect a qualitative pattern of precipitation without expecting exact correspondence of pH or temperature. Aside from these qualitative predictions, we can expect kinetic effects to prevent some of the predicted materials from precipitating.

We have surveyed the effects of altering the pH, oxidation state, and

temperature of Sinclair #4 and Magma-max #1 brines. Under oxidizing conditions, massive quantities of silicates and oxides are predicted to precipitate from both brines, but no sulfides appear. For reducing brines, iron-rich silicates, hydroxides, oxides, and native metals are predicted to coprecipitate with a host

Fig. 12. Precipitation of native copper from Sinclair #4 brine as a function of pH and temperature.

of sulfides, depending on pH. The nature and quantity of all phases change as a function of the brine composition of the wells. Native silver and argentite, for example, are predicted to precipitate from Magmamax #1 brine, but not from Sinclair #4 brine.

As mentioned previously, the HH code predicted the precipitating sulfide assemblage in the Magmamax #1 brine. In recent field tests of the same brine, the nature of scale deposits formed in an expansion

nozzle were analyzed (Fig. 19).

When observed scale constituents were compared to those predicted by the HH code (Table 5) it was apparent that this observed suite of minerals was consistent with the code results.

However, other sulfides such as pyrrhotite, bornite, and wurtzite, as well as a host of silicates, are predicted by the code, but none of these minerals seems to appear in the Magmamax field tests. What does precipitate is an amorphous, iron-rich silica scale matrix which contains Mn, traces of Al, and other constituents. This may either be due to

- Poor thermodynamic data for these compounds in the code's data base
- Complete absence of these phases in the data base
- Kinetic limitations in the precipitation of silicate mineral phases

However, the prediction of numerous Fe-Na-Mg silicate assemblages is an indication that some combination of these ions and silica has a lower Gibbs free energy than silica itself. It is, then, not surprising that an iron-rich silica phase is present.

In addition, our predictions for the suppression of sulfide precipitation in the Magmamax well (pH < 3.5 at 200°C) are in good agreement with

the recent field tests at the San Diego Gas & Electric site. Grens and Owen (1976) reported that when

Magmamax brine "was acidified to pH 1.5, 2.3, and 4.0, scaling in nozzles was eliminated."

Fig. 13. Precipitation from the Magmamax #1 brine as a function of pH, oxidation state, and temperature (60°C). (See Appendix B for meaning of numbers.)

Fig. 14. Precipitation from the Magmamax #1 brine as a function of pH, oxidation state, and temperature (100°C). (See Appendix B for meaning of numbers.)

Fig. 15. Precipitation from the Magmamax #1 brine as a function of pH, oxidation state, and temperature (150°C). (See Appendix B for meaning of numbers.)

Fig. 16. Precipitation from the Magmamax #1 brine as a function of pH, oxidation state, and temperature (200°C). (See Appendix B for meaning of numbers.)

Fig. 17. Precipitation from the Magmamax #1 brine as a function of pH, oxidation state, and temperature (250°C). (See Appendix B for meaning of numbers.)

Table 4. Sulfide assemblage at various temperatures (MagmaMax #1 brine – reducing conditions).

Temperature, °C				
60°	100°	150°	200°	250°
chalcocite (2) ^a	chalcocite (2.5)	pyrrhotite (3.5)	pyrrhotite (3.5)	pyrrhotite (3.5)
chalcocite (2)	sphalerite (2.5)	galena (3.5)	galena (4.5)	galena (5)
bornite (2)	galena (2.5)	sphalerite (4)	sphalerite (5)	sphalerite (5.5)
sphalerite (2.5)	bornite (2.5)	chalcocite (4)	chalcocite (5)	wurtzite (6)
galena (2.5)	pyrite (3.5)	bornite (4.5)	pyrite (5.5)	chalcocite (6)
pyrite (2.5)	pyrrhotite (3.5)	wurtzite (4.5)	wurtzite (5.5)	
wurtzite (3.5)	chalcocite (3.5)	pyrite (4.5)	bornite (6)	
pyrrhotite (4)	wurtzite (4)	chalcocite (5.5)	chalcocite (8)	
argentite (4)	argentite (6)	argentite (10)		
covellite (4.5)				

^aThe numbers in parentheses denote the pH of the brine when that particular mineral first appeared (pH is increasing).

Fig. 18. Precipitation of natural silver and copper from MagmaMax #1 brine as a function of pH and temperature.

Fig. 19. Nature of scale deposits formed in a 8:1 expansion nozzle at Magmamax #1 well as a function of temperature (after L. Owen, private communication, 1976).

Table 5. Observed and predicted sulfide assemblages precipitating from Magmamax #1 brine as a function of temperature, pH, and Eh.

T, °C	Eh	pH (calc)	Predicted	Observed
250	Reducing	4-5	FeS + PbS + ZnS + ZnS (hexagonal) + CuFeS ₂	—
200	Reducing	4-5	FeS + PbS + ZnS + CuFeS ₂ + FeS ₂ + ZnS (hexagonal) + Cu ₅ FeS ₄ + Cu ₂ S	CuFeS ₂ + PbS + ZnS + Cu ₂ S + Fe-rich amor- phous silica matrix. Ag content above back- ground (218°-210°C)
150	Reducing	4-5	FeS + PbS + ZnS + CuFeS ₂ + FeS ₂ + Cu ₅ FeS ₄ + ZnS (hexagonal) Ag ₂ S + Cu ₂ S	Sulphide-deficient, iron-rich, amorphous silica matrix
100	Reducing	5-6	CuFeS ₂ + ZnS + PbS + Cu ₅ FeS ₄ + FeS + Cu ₂ S + FeS ₂ + ZnS (hexagonal) + Ag ₂ S	PbS + Cu ₂ S in iron- rich, amorphous silica matrix. Ag content is high (130°-110°C)
60	Reducing	5-6	Cu ₂ S + CuFeS ₂ + Cu ₅ FeS ₄ + ZnS + PbS + FeS ₂ + ZnS (hexagonal) + FeS + Ag ₂ S + CuS	—

IV. Future Program Applications

A. SCALE-SOLID CALCULATIONS

It is gratifying that the HH code predictions have agreed so well with the field tests at the Sinclair #4 and Magmamax #1 wells — but much remains to be done. Our next step is to expand the pH, Eh (oxidation potential), temperature, and pressure régimes to include more realistic well conditions as well as compositions at various locations within power plants. We will also use field data to check the validity of the existing data base. As we improve the chemical analyses for Magmamax #1 brines, we will have to compare the new brine concentrations using selected check reruns. We will also have to examine other wells in the SSGF possessing different brine compositions and steam qualities.

Other possible experiments that would be of some interest include:

- Partially oxidizing the brine by adding O_2 , Cl_2 , or H_2O_2
- Adding oxidized, low-pH brines from holding ponds to acidify and partially oxidize wellhead brine without adding fresh chemicals
- Determining thresholds for salt precipitation as a function of changes in steam quality, extent

of flushing, oxidation state, temperature, and amount of chemical additives

B. CORROSION

Because the SSGF brines are so highly saline (Table 1), the usual generalizations about corrosion resistance may not be valid. The HH code can calculate concentrations of the various ionic species in equilibrium with Fe, Fe oxides, Ti alloys, etc., as a function of Eh, pH, and temperature. The results can then be used to prepare Pourbaix diagrams for various pipe, separator, nozzle, and turbine materials. These Pourbaix diagrams are conventionally used as a guide to corrosion resistance and choice of materials.

Reservations about kinetics as well as the validity of available thermodynamic data, previously discussed in the first section also apply here. Other important variables are surface structure and porosity. Although the code does not consider these variables as input parameters, it may help assess the importance of various physiochemical parameters. For corrosion calculations, it will be necessary to extend the code's data

base to include appropriate metal oxides. Much data will undoubtedly have to be estimated.

C. REINJECTION

After passing through the energy conversion steps in the power plant and losing its enthalpy, the brine is cool (ambient temperature), its pressure is lower, and it has lost CO_2 and H_2S . This "spent" brine may precipitate additional solids in holding ponds, but, ultimately, it must be pumped back into the geothermal reservoir. Because of this, the reaction between the purged brine and the geothermal reservoir rocks may be significant and should be explored as a function of temperature, pH, and pressure.

The biggest reinjection problem is that pores in reservoir rocks can become mechanically or chemically plugged. Mechanical plugging occurs when pores close and collapse as a result of particles, entrained solids, etc., failing to pass through the pores, or when clays — such as montmorillinites — swell as a result of mineral-solution exchange processes and neck down the pore channels.

Chemical plugging will probably dominate at the higher temperatures encountered deeper in the geothermal reservoir. It can arise either by 1) further precipitation of solids from reinjected brine that has come

into contact with various minerals of the reservoir rocks or by 2) solution of the rocks and reprecipitation of a different mineral assemblage in equilibrium or local equilibrium at elevated pressures and temperatures.

There are at least three ways to reinject spent brine into the geothermal reservoir

- Direct reinjection (including additives to prevent scaling)
- Reinjection after a storage period in holding ponds, resulting in the inevitable oxidation of spent brine
- Reinjection after the addition of other additives has "purified" the brine, thereby avoiding overt mechanical plugging

It is obvious that the HH code can screen these processes.

D. MINERAL RECOVERY

Once a scale-free brine has cycled through the power plant, some of the minerals may be recovered by inducing scale formation or precipitation. This can be done, for example, by adding sulfides or basifying. Thus, the overall total flow plan of extracting power from Salton Sea geothermal brine may become cheaper if some of the Mn, Ag, Pb, Cu, or Li can be recovered (see Fig. 17 for the systematics of Ag and Cu precipitation from Magmamax #1 brine as a function of pH and temperature).

V. Code Improvements

As noted in Section II, the HH code consists of three basic parts

- Calculations
- Activity coefficient approximations
- Thermodynamic data

Each component can be improved to more effectively handle the problems discussed in Section II.

At the outset, we recommend a complete redesign of the thermodynamic equilibrium portion of the code. It should employ a different logic design and be in accord with modern numerical analysis techniques. This would simplify the structure, speed up the calculation, and reduce the memory storage requirement. An equilibrium code with these properties would then be useful as a subroutine for nozzle flow, plant design calculations, and ancillary computations in other energy-related laboratory programs. This subroutine could also be used in a more efficient program to solve the original rock-solution problem. Furthermore, the newly designed code would be sufficiently flexible and general to handle cases in which a saturated brine

was continuously cooled and flashed and to determine the effect on ionic concentrations, pH, and Eh when an arbitrary constituent or solution was added to another solution. Such a code design has recently been proposed by H. B. Levine. A detailed technical review that we made with the assistance of personnel from LLL's Computation Department has led us to recommend the Levine concept. The result should be a more effective computational vehicle, which can be used to carry out Helgeson's original program, as well as to meet the needs of LLL's geothermal program.

We also propose to investigate the activity coefficient approximations for concentrated solutions now being worked on by many people, including Professors Helgeson and Pitzer at Berkeley. The best of these will then be incorporated into our version of the code.

Finally, parts of the data base need updating, and new materials which are of specific geothermal interest must be added. We are currently working with Professor Helgeson in this area.

VI. Acknowledgments

We are particularly grateful to C. Herrick, Los Alamos Scientific Laboratory, who helped us get his version of the Helgeson code running, and D. Norton of the University of

Arizona for useful discussion. We also thank Jack Mathews and Fred Fritsch of LLL for their assistance in reviewing the code design of H. Levine.

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VII. Appendix A

C. Herrick's version of the Helgeson program, PATHCALC, was compiled with the PUTT compiler on a CDC 7600 computer at LLL. PUTT is an updated version of CDC's CHIP (or "RUN") compiler. Herrick had compiled the Helgeson code on a Los Alamos modified version of a CDC Fortran compiler.

Following is a listing of the changes made on Herrick's code. The changes were made so that PUTT would compile the source deck, and the object deck would execute on the CDC 7600 (line numbers refer to the source listing of PATHCALC modified to run at LLL):

1. Line 1. The PROGRAM CARD.

```
PROGRAM PTCALC(INP,YOUT,DATAS,TAPE5=INP,TAPE6=DATAS,TAPE10=YOUT)
```

The logical device assignments are:

5 = input file, INP

6 = data file, DATAS

10 = output file, YOUT

All the files are disk files.

The output file, YOUT, is created at run time by the following system call (before the first WRITE statement):

```
Line 95  LENTH=200000B
```

```
Line 96  CALL DEVICE(6HCREATE,4HYOUT,LENTH)
```

Obviously, the above is very installation-dependent.

2. The following coding was deleted from Herrick's version by making it into comments. The reason for the deletion was that PUTT did not recognize the commands:

```
Line 34  LEXT ALOG10,ALOG,EXP
```

```
Line 35  LCM/ECS/ECSPACE(100000)
```

```
Line 95  CALL JOBNAME(dd(1)) $ CALL DATAS(DD(3))
```

```
Line 97  output of job name and date.
```

```
Line 100 IF (EOF,60) 2225,105
```

Lines 34 and 35 are not necessary with PUTT.

3. Line 1749 was changed to SUMD=0.0 and SUMD was declared a double precision variable: Line 45 DOUBLE SUMD

No attempt was made to improve or correct Herrick's code because of the lack of a comprehensive test input data and its results. There are obvious ambiguities, such as lines 1831 to 1835:

EPS=1.E-10

EPS=1.E-8

EPS=1.E-7

EPS=1.E-4

EPS=1.E-6

Even when the code is run on a CDC 7600, different compilers and math libraries will produce different numbers in the final as well as intermediate result.

MSG/gw/vt

GPO 789-009/7946

XI. Appendix B

1. MnO_2	- pyrolucite	31. Cu_5FeS_4	- bornite	55. $\text{NaAlSi}_3\text{O}_8$	- low albite
2. SiO_2	- quartz	32. FeS	- pyrrhotite	56. $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	- muscovite
3. SiO_2	- silica glass	33. PbS	- galena	57. $\text{NaAlSi}_3\text{O}_8$	- high albite
4. $\text{Fe}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	- minnesotaite	34. Cu_2S	- chalcocite	58. $\text{NaAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	- paragonite
5. Fe_2O_3	- haematite	35. FeS_2	- pyrite	59. $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$	- halloysite
6. Fe_3O_4	- magnetite	36. $\text{Mg}(\text{OH})_2$	- brucite	60. $\text{AlO}(\text{OH})$	- boehmite
7. $\text{Fe}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$	- greenalite	37. $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$	- pyrophyllite	61. $\text{Al}(\text{OH})_3$	- gibbsite
8. $\text{Fe}(\text{OH})_3$	- ferric hydroxide	38. $(\text{Na,Ca})_4\text{Al}_3(\text{Al,Si})_3$ $\text{Si}_6\text{O}_{24}(\text{Cl,CO}_3,\text{SO}_4)$	- marialite	62. $\text{CaAl}_2\text{Si}_2\text{O}_8$	- anorthite
9. Fe_2SiO_4	- fayalite	39. KAlSi_3O_8	- microcline	63. $\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$	- alunite
10. MgFe_2O_4	- magnesioferrite	40. $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$	- kaolinite	64. $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	- analcite
11. $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	- talc	41. $(1/2\text{Ca,Na})_{0.7}(\text{Al,Mg,Fe})_4$ $(\text{Si,Al})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$	- Na-montmorillinite	65. $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$	- zoisite
12. $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	- tremolite	42. $\text{K}_{y<2.0}(\text{Si}_{8-y}\text{Al}_y)$ $(\text{Al}_4\text{Fe}_4\text{Mg}_4\text{Mg}_6)\text{O}_{20}(\text{OH})_4$	- illite	66. $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	- almandine
13. $\text{CaMgSi}_2\text{O}_6$	- diopside	43. Al_2SiO_5	- kyanite	67. KAlSi_2O_6	- leucite
14. $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$	- andradite	44. KAlSi_3O_8	- high sanidine	68. ZnS	- würtzite
15. $\text{Fe}(\text{OH})_2$	- ferrous hydroxide	45. KAlSi_3O_8	- adularia	69. $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$	- phlogopite
16. $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$	- sepiolite	46. $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$	- dickite	70. $(\text{Na,K})\text{AlSiO}_4$	- nepheline
17. $\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$	- chrysotile	47. $(1/2\text{Ca,K})_{0.7}(\text{Al,Mg,Fe})_4$ $(\text{Si,Al})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$	- K-montmorillinite	71. MgAl_2O_4	- spinel
18. MgSiO_3	- enstatite	48. $(1/2\text{Ca,Na})_{0.7}(\text{Al,Mg,Fe})_4$ $(\text{Si,Al})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$	- Ca-montmorillinite	72. $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	- pyrope
19. CaSiO_3	- wollastonite	49. $(1/2\text{Ca,Na})_{0.7}(\text{Al,Mg,Fe})_4$ $(\text{Si,Al})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$	- Mg-montmorillinite	73. Ag	- silver
20. Mg_2SiO_4	- forsterite	50. $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	- alteration muscovite	74. Ag_2S	- argentite
21. FeO	- wüstite	51. Al_2SiO_5	- andalusite	75. $\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$	- Mg-chlorite
22. $\text{Ca}_3\text{MgSi}_2\text{O}_8$	- merwinite	52. Al_2SiO_5	- sillimanite	76. $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	- alteration talc
23. CaMgSiO_4	- monticellite	53. ZnS	- sphalerite	77. MgO	- periclase
24. $\text{Ca}_2\text{MgSi}_2\text{O}_7$	- ackermanite	54. Al_2O_3	- corundum	78. CaO	- lime
25. MgSiO_3	- ortho-enstatite			79. Cu_2O	- cuprite
26. $\text{Ca}(\text{OH})_2$	- portlandite			80. CuS	- covellite
27. $\text{CaFeSi}_2\text{O}_6$	- hedenbergite			81. CaSO_4	- anhydrite
28. Cu	- copper			82. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	- gypsum
29. $\beta\text{-Ca}_2\text{SiO}_4$	- larnite			83. $\text{K}_2\text{Fe}_6(\text{Al}_2\text{Si}_6)\text{O}_{20}(\text{OH})_4$	- annite
30. CuFeS_2	- chalcopyrite			84. H^+	- hydrogen ion