

## Geochemical Equilibrium Codes: A Means of Modelling Precipitation Phenomena in the Salton Sea Geothermal Field

by

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### ABSTRACT

We have used the Helgeson-Herrick geochemical code to predict which minerals will precipitate from Salton Sea Geothermal Field brines. The code's predictions of sulfide-amorphous silica precipitation from the Magmax No. 1 brine are in good agreement with field tests of scaling, although the observed silicate scale matrix is in amorphous form, rather than the numerous crystalline forms 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.

### INTRODUCTION

A major goal of the LLL geothermal project is to develop a total flow concept for converting to electric power the thermal energy of high-temperature, high-salinity brines—found in the Salton Sea Geothermal Field (SSGF). LLL's approach to the total flow process calls for passing the entire wellhead product through stationary, specially

References and illustrations at end of paper.

designed nozzles to form high-velocity jets. These jets then turn an axial-flow impulse turbine that generates electricity.<sup>1</sup> 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.<sup>2</sup>

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 No. 4 and Magmax No. 1 wells. The brine solutions are very concentrated (4-5 molal, ionic strength 5-6), containing mostly NaCl. There are also significant amounts of Ca<sup>2+</sup> and K<sup>+</sup>, as well as H<sub>4</sub>SiO<sub>4</sub>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>, S<sup>2-</sup>, CO<sub>2</sub>, and H<sub>2</sub>S. Clearly, the precipitation of silica and metal sulfide scale is of special interest because of the scale's harmful 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 brines, the laboratory has also employed geochemical-equilibrium codes that can model numerous simultaneous reactions. Geochemical code models, in principle, 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 experiments, and account for differences between various wells or changes in any given well as a function of time.

A large geochemical code is absolutely necessary to treat complex, dirty natural systems such as SSGF brines. In this paper, we use the Helgeson-Herrick geochemical code to investigate solubility relations in the Sinclair No. 4 and Magmamax No. 1 brines. We previously described this code in more detail,<sup>3</sup> checked solubility in the systems NaCl, KCl, and KCl-NaCl in water, and outlined future applications of the code.

Checking the solubilities of simple salt systems showed relatively poor agreement with the specific data points, but did reflect the trends with composition and temperature.<sup>3</sup> Consequently, the code can be used to provide a general survey of the effects of pH and oxidation state. Thus, we can 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.

It is important to recognize that kinetics play a powerful role in determining what actually precipitates as compared to what is thermodynamically possible. Moreover, inevitable imperfections in the data base and activity coefficient approximations may distort the thermodynamic predictions. Consequently, frequent comparison and interaction with field or laboratory experiments are vital to provide consistency. Once such 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.

## RESULTS

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

No. 4 well as input (Table 1). We have studied the minerals that 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). 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 (see Figs. 7 through 11 in Miller *et al.*<sup>3</sup> for a more detailed description of all silicate phases predicted to precipitate). Under reducing conditions, however, the HH code predicts that sulfides and silicates can precipitate as a function of pH and temperature. The sulfide assemblages predicted 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 No. 4 brine under reducing conditions (Fig. 1).

We also have 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 No. 1 well as input (Table 1). We have studied the minerals that 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 again are meant to be boundary conditions (Table 2). 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 always among the earliest precipitates predicted under oxidizing conditions (see Figs. 13 through 17 in Miller *et al.*<sup>3</sup> for a more detailed description of all silicate phases predicted to precipitate).

For a reducing brine, the HH code predicts that a host of sulfides can coprecipitate with a cortege of silicates, oxides, and native metals as a function of pH and temperature. Table 4 shows the predicted 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 No. 1 brine under reducing conditions. Fig. 2 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 than copper at temperatures less than 150 °C.

### CONCLUSIONS

We have used the HH code to investigate solubility relations in the Sinclair No. 4 and Magmamax No. 1 brines as a function of pH, oxidation state, and temperature. Under oxidizing conditions, massive quantities of silicates and oxides are predicted to precipitate from both brines, but no sulfides should appear. For reducing brines, iron-rich silicates, hydroxides, oxides, and native metals are predicted to coprecipitate with a host of sulfides, depending on pH. The nature and quality 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 No. 1 brine, but not from Sinclair No. 4 brine.

As mentioned previously, the HH code predicted the precipitating sulfide assemblage in the Magmamax No. 1 brine. In recent field tests of the same brine, the nature of scale deposits formed in an expansion nozzle were analyzed (Fig. 3). When observed scale constituents were compared with 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 that 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, and 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 not surprising, then, 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<sup>4</sup> reported that when Magmamax brine "was acidified to pH 1.5, 2.3, and 4.0, scaling in nozzles was eliminated." The elimination of the silica scaling at these lower pH's is due to the inhibiting effect of H<sup>+</sup> on kinetics.<sup>2</sup>

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

Table 2. Brine conditions.

	Oxidizing	Reducing
SO <sub>4</sub> <sup>-2</sup>	$2.4 \times 10^{-4}_m$	$1 \times 10^{-30}_m$
S <sup>-2</sup>	$1 \times 10^{-30}_m$	$2.4 \times 10^{-4}_m$

Table 3. Predicted sulfide assemblage at various temperatures (Sinclair #4 brine--reducing conditions).

	Temperature, °C				
	60°	100°	150°	200°	250°
chalcocite (2) <sup>a</sup>	chalcopyrite (3)	pyrrhotite (3.5)	pyrrhotite (3.5)	pyrrhotite (3.5)	
chalcopyrite (2)	bornite (3)	chalcopyrite (4)	galena (4.5)	galena (5)	
bornite (2)	pyrrhotite (3.5)	galena (4)	chalcopyrite (5)	chalcopyrite (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)		

<sup>a</sup>The numbers in parentheses denote the pH of the brine when that particular mineral first appeared (pH is increasing).

Table 4. Predicted sulfide assemblage at various temperatures (Magmamax #1 brine--reducing conditions).

Temperature, °C				
60°	100°	150°	200°	250°
chalcocite (2) <sup>a</sup>	chalcocopyrite (2.5)	pyrrhotite (3.5)	pyrrhotite (3.5)	pyrrhotite (3.5)
chalcocopyrite (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)	chalcocopyrite (4)	chalcocopyrite (5)	wurtzite (6)
galena (2.5)	pyrite (3.5)	bornite (4.5)	pyrite (5.5)	chalcocopyrite (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)				

<sup>a</sup>The numbers in parentheses denote the pH of the brine when that particular mineral first appeared (pH is increasing).

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

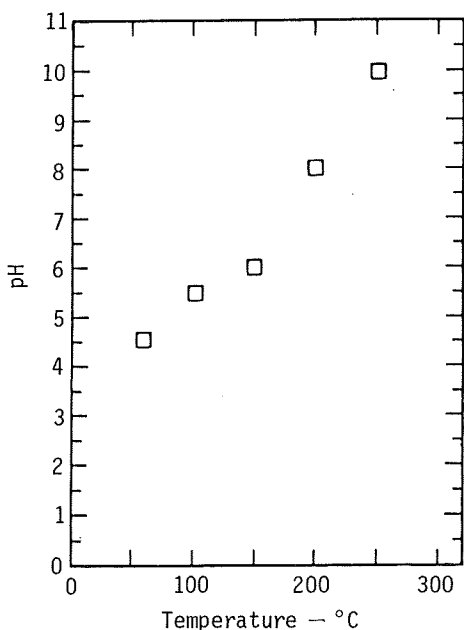


Fig. 1 - Precipitation of native copper from Sinclair #4 brine as a function of pH and temperature.

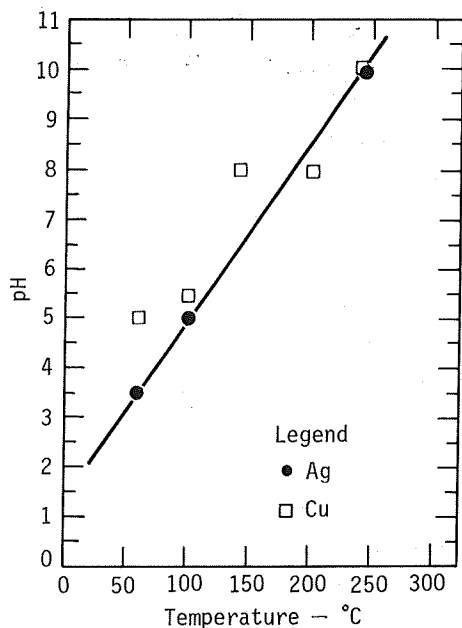
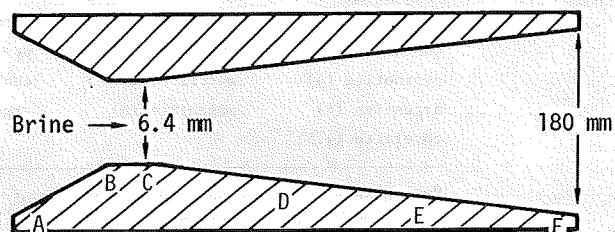


Fig. 2 - Precipitation of natural silver and copper from Magmamax #1 brine as a function of pH and temperature.



Site	T, °C	Scale description
A	218	CuFeS <sub>2</sub> in iron-rich, amorphous silica matrix
B	215	Massive PbS with a basal layer of CuFeS <sub>2</sub> in iron-rich amorphous silica matrix
C	210	Sharp vertical discontinuity between massive PbS and ZnS deposits with lesser amounts of Cu <sub>2</sub> S and a basal layer of iron-rich amorphous silica matrix. Ag content increases over background.
D	150	Sulfide-deficient, iron-rich, amorphous silica matrix
E	130	Dispersed PbS and Cu <sub>2</sub> S in iron-rich, amorphous silica matrix. Ag content is relatively high.
F	110	Same as in zone E

Fig. 3 - Nature of scale deposits formed in 8:1 expansion nozzle at Magmamax #1 well as a function of temperature (after L. Owen, private communication, 1976).