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**STUDIES OF BRINE CHEMISTRY, PRECIPITATION
OF SOLIDS, AND SCALE FORMATION AT THE
SALTON SEA GEOTHERMAL FIELD**

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ABSTRACT

We investigated factors affecting the precipitation of solids and deposition of scale from the hypersaline brines of the Salton Sea geothermal field—two potential problems in the proposed utilization of these brines for electric power generation. We determined the average physical and chemical composition of the fluid from Magma-max No. 1 well and noted the effects of changes in well flow rate on the chemistry of the brine and the formation of solids. We also studied the effects of pH on the process stream chemistry and on the composition and rates of formation of solids and scale that precipitated from this brine. Reduction of the pH from 6 to 4-5 decreased the scaling rates and increased the proportions of barium sulfate and calcium fluoride in the scales and precipitated solids. These studies were conducted using a small-scale four-stage brine flash system constructed at the site.

INTRODUCTION

Several important potential problems in the utilization of the hypersaline brines of the Imperial Valley for electric power generation are under investigation by the Lawrence Livermore Laboratory (LLL). One is the development of techniques for minimizing or controlling the precipitation of solids and deposition of scale from the brine as it cools. Another is the selection of materials that resist corrosion and erosion by the hot, highly saline brine. Progress in these and other areas, including brine disposal, energy conversion technology design studies, and geological investigations, has been reported.¹⁻⁷

In the summer of 1977, a small-scale (6 gpm) four-stage brine flash system was constructed at the

Niland test site; brine was supplied from Magma-max No. 1 well. The system was used to determine the effect of modest pH reduction on scaling rates, materials response, the chemistry of the process streams, and the composition of suspended solids and scales. The effluent brine was also used in a series of off-line bench tests of organic additives for scale control³ and to measure baseline rates of precipitation of solids. During this time, a number of analyses of the geothermal fluids (with and without acidification) and solids were carried out, and these are reported here. Preliminary reports of the results have already appeared,²⁻⁶ and others will be forthcoming.⁷

FOUR-STAGE FLASH SYSTEM

A simplified diagram of the LLL Four-Stage Flash System is shown in Fig. 1. In addition to the brine sampling ports shown, there were also ports in the brine bypass for sampling brine and steam from the first-stage separator and ports for sampling steam from the second- and third-stage flash tanks.

Each of these ports was connected to a stainless-steel or zirconium cooling coil for cooling the samples to ambient temperature.

Also not shown in Fig. 1 is apparatus connected at various times to the experiment station. This included a section of large-diameter pipe

Fig. 1. The LLL geothermal four-stage flash system.

through which a portion of the brine flowed. The effect of this "delay line" was to "age" the brine an additional 20 minutes to simulate the residence time of brine in the injection line of the San Diego Gas and Electric Company Geothermal Loop Experimental Facility (GLEF). A slotted metal cylinder

was connected to the delay line to simulate the slotted liners in the completion interval of the injection well. Apparatus for core flooding experiments and additional corrosion-measurement equipment were also connected at various times to the experiment station.

MAJOR PARAMETERS OF THE BRINE COMPOSITION

The LLL four-stage flash system was first operated intermittently from August to November 1977. Baseline data on the precipitation of solids (largely silica) from the effluent brine as a function of pH were obtained.⁶ During this time, measurements were also made to determine the optimum pH for the 30-day corrosion test, and the first tests of organic additives for scale control³ were carried out. It became evident during this period that the composition of the brine changed considerably with the flow rate of the well. It was observed that the composition of the fourth-stage effluent brine that we usually monitored changed markedly, depending upon whether or not the GLEF was also drawing fluid from the well (Tables 1-3). Full flow of Magmamax No. 1 to the GLEF

Table 1. Total dissolved solids in Magmamax No. 1 effluent brine (105°C, 1 atm).

Date	Density at 25°C, g/cm ³	Total dissolved solids, wt%	GLEF in operation
1977			
Sept. 17	1.141	19.0	No
Sept. 19	1.145	19.9	No
Sept. 21	1.143	19.4	No
Sept. 22	1.172	22.5	Yes
Oct. 23	1.149	21.2	No
Dec. 5	1.142	19.7	No
Dec. 14	1.174	22.7	Yes
1978			
Feb. 3	1.170	22.4	^a
Feb. 3 (Third stage)		21.3	
Feb. 3 (Second stage)		20.3	
Feb. 3 (First stage)		19.1	

^aSee Table 2.

Table 2. Gross composition of effluent brine sampled directly at fourth stage at 105°C during the 700-hour corrosion and scaling test.

Date	Time	pH	Chloride, M	Density at 25°C, g/cm ³	Initial SiO ₂ , mg/kg	GLEF in operation
Dec. 4, 1977	1440	6.00	3.68		464	No
Dec. 5	1130	6.00	3.78	1.142	450	No
Dec. 6	1030	5.45			450	No
Dec. 6	1345	5.00	4.06			No
Dec. 7	1445	5.08	4.20		502	No
Dec. 8	0910	4.53	4.60		595	Yes
Dec. 8	1600	5.02	4.50			Yes
Dec. 9	0920				540	Yes
Dec. 9	1030	4.83	4.05			Yes
Dec. 9	1600	4.65	4.38			Yes
Dec. 10	0700	4.37	4.41			Yes
Dec. 13	1400				558	Yes
Dec. 13	1700		4.44			Yes
Dec. 14	0915	4.92			437 ^a	Yes
Dec. 14	1100	4.85	4.46	1.174	562	Yes
Jan. 19, 1978	1000	3.94				No
Jan. 19	1345		3.13			No
Jan. 19	1530	4.42		1.131	444	No
Jan. 20	0900	4.20	3.26	1.131	444	No
Jan. 20	1430		3.36			No
Jan. 21	0900		3.55		420	No
Jan. 22	1430	4.34	4.16	1.164	489	Yes
Jan. 23	1400	4.77	4.06	1.161	507	Yes
Jan. 24 ^b	1400	5.00	3.63	1.149	515	Yes
Jan. 25	0745	3.51	4.02			Yes
Jan. 25	1000	3.48		1.158	490	Yes
Jan. 25	1400	3.65	4.14	1.163		Yes
Jan. 26	Plant shutdown					No
Jan. 27	1640	4.38	3.75	1.148	515	No
Jan. 28	1315	4.20	4.03	1.161	489	Yes
Jan. 29	1115	4.50	4.12	1.161	485	Yes
Jan. 30	1440	3.41	4.49	1.173	521	Yes
Jan. 31	0750		4.48			Yes
Jan. 31	0833	4.14	4.46	1.171	548	Yes
Feb. 1-2	Plant shutdown					
Feb. 3	1400	3.90	4.31	1.170 ^c	548	No ^d
Feb. 3	1700	4.09		1.152		No
Feb. 4	0830	4.52	3.91	1.160	526	No
Feb. 4	1450	4.20	4.74	1.180 ^e		Yes ^f
Feb. 4	1630			1.175	546	Yes ^g
Feb. 5	1600	3.82	4.27	1.172	546	Yes
Feb. 6	0900	4.03	4.40	1.172 ^c	566	No ^h
Feb. 7	0820	3.92	4.14	1.160	522	No
Feb. 8	0900	4.16	4.05	1.158	517	No
Feb. 8	1615	3.75	4.27	1.169		No
Feb. 9	1127	3.70	4.04	1.167	528	No
Feb. 10	1100	3.75		1.165	520	No
Feb. 12	1500		3.95	1.158	462	No
Feb. 13	0815	4.08	3.77	1.159	511	No

^aAcid off for 1 hour just prior to sampling.

^bPoor pH control this day.

^c"Strong" brine persisted for several hours.

^dOff at 0900.

^eMaximum observed chloride concentration and density.

^fOn at 1300.

^gUSBM operated sporadically from Feb. 4 to Feb. 10.

^hOff at 0700.

Table 3. Parameters of geothermal brine for statistical analysis.

						Analysis after >30 d incubation at 90°C	
Sample Date	pH	Chloride, <i>M</i>	Density at 25°C, g/cm ³	Initial SiO ₂ , mg/kg	GLEF in operation ^a	SiO ₂ in filtrate, mg/kg	Solids, mg/kg
1977							
Sept. 19	2.9	3.65	1.145	453	No	187	379
21	5.1	3.70	1.143	464	No	191	382
Dec. 4	6.0	3.66	1.140	465	No	178	440
7	5.1	4.20	—	502	No	146	500
8	5.2	4.55	—	585	Yes	143	581
14	4.9	4.46	1.174	552	Yes	143	573
1978							
Jan. 21	4.4	3.55	—	420	No	170	361
22	4.4	4.16	1.164	489	Yes	184	502
25	3.8	4.14	1.163	490	Yes	175	483
28	4.2	4.03	1.161	489	Yes	166	491
29	4.1	4.12	1.161	485	Yes	171	468
Feb. 3	4.1	—	1.152	—	No	173	387
4	4.2	4.74	1.175	546	Yes	146	551
6	4.0	4.40	1.172	566	No	173	491
7	3.9	3.92	1.160	522	No	162	453

^aNo = 0, Yes = 1 in statistical analysis.

was in the range of 300,000 to 400,000 pounds per hour whereas the flow capability of the LLL apparatus (including bypass) was only one-tenth of that amount.

Because of brine composition fluctuations, the effect of GLEF operation on fluid composition was monitored during the 30-day (700-hour) corrosion test begun in December. The major parameters of the LLL system effluent brine are listed in Tables 1 and 2 with a notation on the status of the GLEF at the time the brine was sampled.

Some of the data in Table 1 are taken from an earlier report⁶; they show that total dissolved solids, chloride concentration, and density of the brine always increased with well flow rate. Except for the small amount of additional data given in Table 1, measurement of total dissolved solids was not performed after the initial shakedown tests of September 1977. The composition of the brine was more accurately indicated by its chloride concentration and density, and these measurements were faster to carry out.

Differences in the pH and concentrations of the major constituents of the brine affect solubil-

ities and influence the rates of precipitation reactions that occur after the brine is flashed. This is illustrated in Fig. 2, which shows the rates of precipitation of silica and formation of suspended solids from brines having a low and a high concentration of chloride. At higher chloride (and total dissolved salt) concentrations, these rates are greater. The total quantity of solids produced once equilibrium has been attained is also larger for the "stronger" brines, as would be expected from the larger initial concentrations of dissolved silica. However, it also appears that at equilibrium the solubility of silica is lower for the stronger brines.

The relationship between the major parameters of the brines and the rates of solids and silica precipitation was examined in more detail by carrying out a statistical analysis of the various factors involved. Table 3 lists the composition of a series of brine samples taken during the four-stage flash system tests and the results of the determinations of the levels of suspended solids and dissolved silica after long-term (>30 d) incubation⁶ of the brines at 90°C. The effect of GLEF operation was assessed by giving "no" a value of 0 and "yes" a value of 1 in the statistical matrix.

FIG. 2. (a) Concentrations of dissolved silica in filtrate and (b) concentration of filterable solids in brine (pH 5.0) as functions of time after flashing to 105°C.

The results of a correlation analysis (Table 4) show that GLEF operation and its greater well flow rates increased the density, chloride concentration, and amount of long-term suspended solids of the brines. It is also significant, but not obvious from a cursory examination, that there was no correlation between the characteristics of the brine after incubation and the initial pH of the brine. There was a high positive correlation between the suspended solids and the initial SiO₂. Another interesting result was the clear indication that the amount of

SiO₂ in the filtrate, which is the equilibrium solubility of silica, was inversely proportional to the concentration of salts in the brine. This confirms the difference shown in Fig. 2a.

A plot of the solubility of silica as a function of the density of the brine and a linear least-squares fit to the data are given in Fig. 3. A value obtained for Magmamax No.2 well, which produces a stronger brine, is shown for comparison, and this value falls on the line fitted to the solubility data for brines taken from Magmamax No. 1 well. These data on

Table 4. Estimated correlation matrix for the parameters of geothermal brine listed in Table 3.^a

	pH	Chloride concentration	Density	Initial SiO ₂	GLEF	SiO ₂ in filtrate	Solids
pH	1.000	0.032	-0.230	0.105	-0.032	-0.268	0.255
Chloride concentration		1.000	0.951*	0.884*	0.632*	-0.709*	0.926*
Density			1.000	0.872*	0.628*	-0.733*	0.875*
Initial SiO ₂				1.000	0.386	-0.669*	0.861*
GLEF					1.000	-0.366	0.718*
SiO ₂ in filtrate						1.000	-0.746*
Solids							1.000

^a1.00 = perfect correlation; an asterisk indicates that the value is statistically different from zero at $\alpha = 0.05$ level.

FIG. 3. Solubility of SiO₂ as function of chloride concentration in Magmamax No. 1 brine at 90°C. One value (triangle) obtained for Magmamax No. 2 is included for comparison, but it was not included in the curve-fitting calculations. Solubility of silica is given on a weight basis; to convert values to a volume basis, multiply the values by the brine density: 1.14 for low concentrations (<4.3 mol/l) and 1.17 for high concentrations (>4.3 mol/l).

the effect of salt concentration on the solubility of silica extend to high concentrations the results obtained by investigators at EIC Corporation.⁸

These workers, who studied the chemistry of silica precipitation in a variety of simulated geothermal brines, also observed the dramatic accelerating effect of dissolved salts on the rate of precipitation of silica. The depressing effect of dissolved salt on the solubility of silica increases the rates of silica scaling from these brines³ and probably affects the accuracy of geothermometer temperature calculations.⁹

The total salt concentration of the brine is reflected very accurately by its density, i.e., there is an almost perfect correlation between the density

and the chloride concentration. Chloride concentrations, in turn, parallel the relative concentrations of most of the minor constituents of the brine (see below). Because the brine density is relatively easy to monitor on-line and in real time with suitable equipment, it appears to be a good parameter for process control.

The causes of the variation of brine composition with well flow rate in the manner observed is open to speculation. However, it appears reasonable that the temperature gradient that must exist downwell could also cause a gradient of increasing fluid salt concentration with depth and that increased well flow rates tap these more concentrated regions.

ELEMENTAL COMPOSITION OF THE BRINE

Three samples of the brine were taken for elemental analysis during the flash system tests. Samples of first-stage separated brine were taken on two different days to represent the two extremes of composition: when the GLEF was operating and when it was not. A sample of the effluent brine from the fourth stage also was taken shortly after sampling the first-stage brine on the day of GLEF operation. The brines were acidified to a concentration of 1% HCl immediately upon sampling.

Historically, there are a number of elements that have always been determined in brines from the Salton Sea geothermal field. To ascertain whether unexpected ones were also present in the flash system samples, the two first-stage samples were evaporated to the solids, and these solids were analyzed by emission spectrography. The results of this analysis for the "less-common" elements are given in Table 5. As can be seen, the concentrations of most of these elements specifically sought are below the detection limits for the technique as indicated by "<" in Table 5. Silver and gallium lines were seen in the analysis, but the values given for these elements in Table 5 are somewhat uncertain and represent the maximum possible concentrations. For elements such as the platinum metals and uranium, the sensitivity of the technique was inadequate for a good analysis; the actual concentrations of these elements were probably two orders of magnitude below the detection limits shown in Table 5.

Table 5. Emission spectrographic analysis of solids from evaporation of first-stage separated brines from Magmamax No. 1.

Element ^a	Estimated concentration in brine, mg/kg	
	Sampled Jan. 20, 1978	Sampled Jan. 31, 1978
Al	6	4
V	2	2
Ga	0.2	0.2
Ag	0.2	0.2
Be, Cr	<0.2	<0.2
Bi, Co, Ni, Yb	<0.6	<0.6
Ti, Zr, In	<2	<2
Er, Eu, Tm	<2	<2
Y, Ge, Pd	<2	<2
Cd, Nb, Sb, Au	<6	<6
Dy, Gd, Ho, La	<6	<6
Lu, Nd, Pr, Sc	<6	<6
Ce, Tl	<6	<6
Pt, Rh, Ru	<20	<20
Sm, Tb, As, W	<60	<60
Th, U, Ta, Hf	<200	<200

^aOnly less-common elements are listed.

A more accurate determination of the most important elemental constituents of the brine was performed by atomic absorption spectrophotometry (AAS) using the method of standard addition. Iron was determined by the 1,10-phenanthroline spectrophotometric method. The brines were also

analyzed by means of a computer-controlled, inductively-coupled-plasma (ICP) emission spectrometer system. A brief study of the accuracy of the ICP technique compared to AAS for these brines has been reported¹⁰; analysis by ICP requires a 20- to 50-fold dilution of the samples.

Table 6 summarizes the results of the analyses of the three geothermal brines. Comparing the two brines sampled at two stages of the plant on January 31, one can see the increase in brine concentration as it was flashed from ~200 to ~105°C and the steam removed. The concentrations of most of the constituents of the brine (except magnesium and strontium) were higher when the GLEF was operating on January 31 than on January 20. Although boron was determined here only by the ICP technique, it appears to be an important constituent and should be included in the primary group for analysis in future work. In general, the levels of most of the elemental constituents found in the present work were similar to those previously reported for Salton Sea geothermal brines.^{11,12}

One element for which an accurate determination was not obtained is barium. The brines sampled during the flash tank tests had been acidified in the plant to pH ~4.5 for the corrosion tests. Under these conditions, high concentrations of BaSO₄ appeared in the low-temperature scales, and this compound also precipitated from the brines after they were sampled but before they were analyzed at Livermore. Thus the concentration of remaining soluble barium was significantly lower than that in the original brine.

This error was not discovered until after conclusion of the flash system tests. On July 21, 1978, during a later period of LLL plant operation (but not of GLEF operation), a new sample of first-stage brine was taken specifically for barium analysis. This sample was immediately diluted with water by a factor of seven, acidified to a concentration of 1% HCl, and analyzed by AAS within two days. The value found in this case was 290 mg/kg (compared to ~90 mg/kg for the flash tank samples); thus Magmamax No. 1 brine probably had concen-

Table 6. Elemental analyses of geothermal brines from Magmamax No. 1.

	First stage at 1115, Jan. 20, 1978	First stage at 0828, Jan. 31, 1978	Fourth stage at 0833, Jan. 31, 1978
pH	6.00	6.12	4.14
Density, g/cm ³	1.128	1.142	1.171
Chloride, M	3.17	3.66	4.46
Element	Determined by atomic absorption spectrophotometry, mg/kg		
Li	110	124	142
Na	44,000	51,000	57,000
K	8,000	9,000	10,000
Rb	44	52	58
Cs	10	11	11
Mg	78	72	84
Ca	16,000	20,000	23,000
Sr	392	341	418
Ba		~300 ^a	
Fe	134 ^b	200 ^b	233 ^b
Cu	0.7	0.9	0.8
Mn	453	596	680
Pb	37	61	61
Zn	201	252	289
Si as SiO ₂	443	469	548
	Determined by ICP emission spectrometry, mg/kg		
Al	<10	<10	<10
As	7	11	13
B	405	440	512
Cd	1.2	1.3	1.5
Co	0.3	0.3	0.4
Mo	4	4	5
Ni	0.2	0.2	0.4
P	7	8	9
Ti	0.4	0.4	0.4
V	0.5	0.6	0.7
Zr	0.3	0.3	0.3

^aSee text.

^bDetermined by visible spectrophotometry.

trations of barium in the vicinity of this value during the flash tank tests. This concentration is about twice that reported previously^{11,12} for this brine, and thus many of the previous analyses may have been subject to the error of BaSO₄ precipitation. The formation of this compound from these brines will be discussed further in connection with the analyses of the precipitated solids.

FOUR-STAGE FLASH SYSTEM pH PROFILE

During operation of the four-stage flash system with acidified brine, control of the brine pH was effected by manual measurement of discrete

samples from various points in the system (Fig. 1). These samples were obtained through ambient-temperature cooling coils permanently installed in

Table 7. Four-stage flash system pH profiles.

Sampling point	pH		
	Unmodified brine ^a	Target pH = 5 ^b	Target pH = 3 ^c
First-stage separated brine	6.14	6.12	6.00
Separated brine downstream from acid injection point	6.10	4.36	2.94
Second-stage brine	6.17	5.54	2.95
Second-stage steam condensate	6.11	5.32	4.79
Third-stage brine	6.09	5.41	2.90
Third-stage steam condensate	6.50	5.68	3.52
Fourth-stage brine (control point)	5.94	5.19	2.83
Output of delay line	5.94	5.40	2.82

^aSept. 20, 1978.

^bSept. 19, 1978.

^cSept. 18, 1978.

the system, and pH values were measured using laboratory pH meters. The brine at the fourth stage (~110°C) was designated as the control point, and the flow of acid was adjusted to achieve the desired pH at this point. This meant that other points in the system would deviate in pH from that at the control point. Thus it was of interest to learn the extent of these deviations. The pH of the fluids at several other points in the system were routinely monitored, and several times during the tests all accessible points were checked.

Typical results of the plant pH measurements are shown in Table 7. The pH values of the steam

condensate fractions were always higher than those of the corresponding brines. This is characteristic of Niland brine flash systems and is due to the presence of ammonia in the condensate. The pH values might have been even higher were it not for the fact that the steam condensates are apparently contaminated by brine (see below). As was sometimes but not always the case, control of the pH at ~5.2 in this experiment (see Table 7) required the pH of the brine to be significantly lower at the point immediately downstream from where the acid was injected.

STEAM CONDENSATE ANALYSES

Several analyses of the steam condensates from the LLL four-stage flash system were carried out. The performance of the first-stage wellhead separator was very good, as indicated on two occasions by the purity of its steam condensate. Chloride concentrations were 10 ± 1 and 38 ± 2 mg/l on October 23, 1977, and January 24, 1978, respectively. Sulfate concentrations at the same time were found to be 6 and 14 mg/l; the presence of sulfate may have been due to the use of irrigation water as a purge liquid. The separator subsequently failed and was found to have accumulated large quantities of calcium sulfate scale.¹³ The concen-

tration of sulfide in the first-stage steam condensate was measured by an ion-selective electrode technique on January 25, 1978, and found to be 43 mg/l. Because the GLEF was operating that day, this value can be regarded as a maximum value. At the same time, the concentration of sulfide in the condensate from the first stage of the GLEF was 33 mg/l.

Measurement of the steam condensate from the second and third stages of the LLL four-stage flash system yielded high values of chloride concentration: 3.00 and 3.50 M (~10⁵ mg/l), respectively, on October 22, 1977. A change in sampling point

did not change these values significantly. These concentrations were not greatly different from those of the brine at these stages of the system, and probably represented significant carryover of brine into the steam phase. It should be noted, however,

that very little liquid brine is required in a large volume of steam to yield a steam condensate high in chloride. Moreover, the flash tanks themselves were not designed or expected to be efficient separators.

ANALYSIS OF SUSPENDED SOLIDS

The concentrations of suspended solids in the fluids of the four-stage flash system were determined in early experiments that have been discussed previously.⁶ The level of suspended solids in the effluent from the fourth stage was generally ~50 mg/kg for unmodified brine and <10 mg/kg for the acidified brines. No determinations of the upstream levels were carried out.

It was noted several times, when the pH of the brine was measured during the acidification experiments, that the separated, 200°C brine sampled downstream from the acid injection point contained

high levels of black suspended solids. These tended to accumulate in the sample tubing, but could be flushed out by a high flow of the sampled brine. Because these particles might have been a cause of material erosion, they were collected and analyzed by x-ray fluorescence spectrometry. The major elements in these suspended solids were, in decreasing concentration, Pb, Fe, Cu, Ag, As, S, Sb, and Si; thus the solids appear to be predominantly silica and the sulfides of Pb, Fe, Cu, As, and Sb—the principal components of high-temperature scale.

ANALYSIS OF PRECIPITATED SOLIDS

During the course of the flash tank experiments, a large number of experiments were performed in which the effluent brine was sampled, sealed under nitrogen in glass ampoules, incubated at $90 \pm 5^\circ\text{C}$, and analyzed to determine the rates of solids and silica precipitation. Baseline information on these rates in unmodified, diluted, and acidified brine was obtained,⁶ and the effects of organic additives on the solids and silica precipitation were later measured.³ In many cases, the solids formed were analyzed by x-ray fluorescence, x-ray diffraction, and emission spectrometry; these results are of interest here.

Table 8 lists several typical examples of the analyses of the solids precipitated from effluent Magmamax No. 1 brine. An examination of these and other data indicates a number of trends. First, the solids from the unacidified brine were nearly pure silica. Second, dilution (~20% by weight) of the brine with pure, deaerated water changed the composition of the solids very little (but did delay silica precipitation and reduce the quantity of solids significantly⁶). Third, acidification of the brine reduced the proportion of iron in the precipitate;

this is reasonable since a lower pH would be expected to decrease the extent of hydrolysis of the iron species.

Probably the most important effect of acidification (note that the brine was acidified in the flash system, not in the laboratory) was that it dramatically increased the concentrations of barium, calcium, and strontium in the precipitated solids. X-ray diffraction analyses indicated that the barium occurred in the form of crystalline BaSO_4 (barite) and that a large fraction of the calcium was found as CaF_2 (fluorite). Both BaSO_4 and CaF_2 were also important constituents of the low-temperature scales that formed from the acidified brines during the flash tank tests (see below).

Barium sulfate has often been found to be a major constituent of other geothermal^{14,15} and oil-well fluid^{16,17} scales, and its solubility has been studied as a function of temperature and salt concentration.^{18,19} A salient feature of the precipitation of BaSO_4 is its tendency to form supersaturated solutions that are slow to reach equilibrium,^{14,16-20} and thus exhibit delayed

Table 8. Composition of solids precipitated from incubated effluent brine.^a

Element	Composition of precipitated solids, wt%			
	Unmodified, pH = 6.0; 3.68 M Cl ⁻	Diluted unmodified brine	Acidified, pH = 3.8; 4.27 M Cl ⁻	Acidified, pH = 5.15; 4.60 M Cl ⁻
Si as SiO ₂	96.9	94.3	85.6	68.7
Li	0.001	b	0.001	b
Na	0.1	b	0.03	b
K	0.6	0.7	trace	0.2
Rb	0.002	0.002	<0.001	0.002
Be	0.0003	b	0.0001	b
Mg	0.003	b	0.002	b
Ca	1.15	1.2	3.3	13.5
Sr	0.003	0.004	0.09	0.4
Ba	<0.05	<0.05	4.2	10.4
B	0.06	b	0.3	b
Al	0.02	b	0.2	b
S	<0.1	<0.1	0.4	1.9
As	0.02	0.03	0.007	0.01
Sb	b	b	0.004	b
Mn	0.08	0.14	0.002	<0.005
Fe	0.98	2.7	0.63	0.60
Ag	0.002	b	0.01	b
Cu	0.016	0.12	trace	0.01
Zn	0.17	0.21		0.03
Pb	0.029	0.062	0.002	0.01
Cl ⁻	<0.1	<0.1	0.28	4.0

^aIncubation for 7-9 d at 90°C.^bNot determined.

precipitation. Solubility also increases with temperature and with salt concentration.^{18,19}

The conditions were not exactly the same as those encountered here, but from the data of Templeton¹⁸ for 4.0 M NaCl at 95°C, the solubility product of BaSO₄ was calculated to be 1.3×10^{-7} (vs 1.0×10^{-10} for pure water at 25°C). Thus, at a Ba²⁺ concentration of ~300 mg/l, precipitation of BaSO₄ should take place at a concentration of SO₄²⁻ greater than ~6 mg/l. At the time this work was done, accurate prompt-sample analyses of the Magmamax No. 1 brine for sulfate did not exist,* but our value was the lower limit of the range of estimates for this and similar reducing

brines in the Imperial Valley.¹² Thus it appeared that solids precipitated from the Magmamax No. 1 brine probably should contain appreciable concentrations of BaSO₄.

A possible source of sulfate in our tests was, as mentioned above, the use of irrigation water to purge the wellhead separator. However, BaSO₄ was never found in the solids from effluent brine that had not been acidified nor from first-stage separated brine obtained upstream from the acidification point, even though these brines had been incubated for a sufficiently long time (>1 week) to reach equilibrium.

The most interesting question is why acidification of the brine markedly increased the concentrations of BaSO₄ in the solids and probably also in the scales. Although we have not found BaSO₄ in solids precipitated from unacidified brine at the

*Stability of the analytical sample is an important factor in the accuracy of the determination, but another problem is obtaining a truly representative sample of the well fluid that is not contaminated by ground water.

LLL facility, it has been found at low concentrations (~2%) in scales formed from unacidified Magmamax No. 1 brine at the GLEF.²¹ It is known that the addition of acid to a supersaturated BaSO₄ solution enhances the growth of large crystals in the precipitate²² (and this may be a factor in our observations), but the long incubation times for the solids measurements should have eliminated the effects of different rates of crystal growth from the comparisons of acidified and unacidified brines.

It is also conceivable that additional sulfate ion was present during the acidification runs because of air oxidation of sulfide in the brine; the air could have been introduced in the 1.5 M hydrochloric acid (ACS reagent grade) solution used for the on-line acidification. Unfortunately, the levels of sulfide in the brine have not been determined accurately; however, chemical model²³ calculations (by D. D. Jackson, LLL) indicated that the concentrations of oxygen existing in the brine as a result of acidification were probably too low to oxidize sufficient quantities of sulfide ion. It appears that further speculation on the origin of the BaSO₄, CaF₂ (and possibly SrSO₄, CaSO₄) in the solids must await more complete measurements of the sulfate and fluoride anion concentrations in the brines and additional experiments with unacidified brine to deter-

mine whether or not these compounds are represented in the long-term composition of Magmamax No. 1 fluids.

The element silver or its compounds have been found frequently to be minor constituents of the solids precipitated from the brine, and somewhat higher concentrations have been measured in scales formed at high temperature. In most of the routine x-ray and emission spectrographic analyses of precipitated solids, the concentration of silver appeared to be on the order of 0.01%, but no careful assays of these solids for silver were done. To obtain a better indication of the typical concentration of precious metals in the precipitated solids and their value as minerals, a large sample of the acidified effluent brine (February 4, 1978; 4.7 M chloride; 1.175 g/cm³ density) was taken, incubated in the usual manner at 90°C for 10 days, and filtered to recover the solids. The solids were then sent to a commercial laboratory that specialized in precious metal assay. The results were silver (<0.001%), gold (<0.005%), and platinum (<0.01%); thus this particular sample had little monetary value. Because effluent brines originating from flash systems are much lower in sulfide ion than the hot upstream fluids, solids and scales formed from the latter should be much more promising sources of silver, especially as Ag₂S.

ANALYSIS OF SCALE SAMPLES

After termination of the flash system operation, during which the test materials had been exposed to acidified brine, the four-stage flash system was disassembled and samples of scale were taken from various locations. A sample of scale was also obtained from the Magmamax No.1 wellhead.

The samples of scale taken from the wellhead, the first-stage separated-brine location, and the delay line had formed on relatively rapidly corroding mild-steel pipe. These samples therefore consisted of a mixture of both corrosion product and "true" scale, i.e., solid material that formed as a precipitate only from the constituents of the brine and then adhered to the surface of a substrate. Samples of scale from the other locations listed in Table 9 more nearly represented "true" scale because they were taken from coupons of Inconel 600, which has been found to be one of the alloy

materials most inert to the effects of acidified geothermal brine.⁷ The scales from these locations and the delay line formed from acidified brine; the wellhead and separated, 200°C-brine scales formed from unmodified brine upstream from the point of acidification.

Before analysis, the samples of scale were crushed and mixed thoroughly in an attempt to obtain a bulk, cross-sectional composition of the material from the top of the scale deposit to the metal substrate. These scales typically varied in composition in cross section,¹ but no attempt was made in the present study to define this. The scale samples also were analyzed in a nearly "as-is" condition, i.e., no attempt was made to remove entrained brine by water washing, and the samples were not heated to dry them beyond the condition reached in the ambient atmosphere.

Table 9. Analyses of scale from Magmamax No. 1 wellhead and the LLL four-stage flash system after ~720 h operation.

Element	Composition, wt%							
	Wellhead, 220°C	Separated unmodified brine, 200-220°C	2nd-stage brine, 150°C	2nd-stage steam, 150°C	3rd-stage brine, 125°C	3rd-stage steam, 125°C	4th-stage brine, 110°C	Delay line, 85°C
Si as SiO ₂	2	27	60	27	64	64	49	39
Li	a	0.1	0.03	0.1	0.03	0.01	0.01	0.1
Na	a	10	3	1	3	3	1	20
K	<0.5	1.6	1.3	1.5	0.64	0.82	0.8	1.4
Rb	<0.1	0.01	0.02	0.02	0.007	0.004	0.003	0.01
Be	a	0.0003	0.001	0.0006	0.0003	0.0003	0.002	0.0001
Mg	a	0.2	0.02	0.02	0.02	0.05	0.03	0.02
Ca	2	4.2	2.0	1.2	2.7	2.9	26	6.1
Sr	trace	0.06	0.04	0.01	0.22	0.03	0.12	0.40
Ba	<0.1	<0.1	<0.1	<0.1	3.5	0.32	1.2	5.3
B	a	0.03	0.03	0.2	0.03	0.05	0.1	0.05
Al	a	0.1	0.3	2	0.1	0.2	0.2	0.02
Y	<1	<0.005	0.01	0.1	<0.005	<0.005	0.02	<0.005
S	12	2.4	<1.0	<1.0	<1.0	<1.0	1.5	2.3
As	a	0.15	0.32	0.97	0.21	0.45	0.07	0.11
Sb	trace	0.019	0.22	0.65	0.11	0.27	0.069	0.083
Ti	0.03	<0.05	<0.05	<0.05	<0.5	<0.05	<0.2	<0.8
Cr	0.09	<0.02	0.03	0.34	<0.2	<0.01	<0.05	<0.3
Mn	0.03	0.67	0.21	0.27	0.12	0.12	0.03	0.12
Fe	0.7	22	7.1	14	2.4	6.0	1.4	0.59
Ni	0.01	<0.01	0.19	1.7	0.07	0.16	0.05	<0.01
Mo	a	<0.002	<0.002	0.004	<0.002	<0.002	<0.002	<0.002
Ag	0.34	0.008	0.028	0.11	0.024	0.056	0.01	0.012
Cu	0.02	1.0	0.4	0.5	0.2	0.6	0.15	0.08
Zn	0.07	0.11	0.04	0.03	0.06	0.09	0.02	0.08
Pb	76	1.3	0.16	0.08	0.55	0.90	0.21	0.25
Cl ⁻	a	7.9	9.9	1.7	7.7	4.3	3.2	18
Br ⁻	a	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
F ⁻	a	a	a	a	a	a	26	a

^aNot determined.

A summary of the analyses of these scales by x-fluorescence and emission spectrometry is given in Table 9. The scale samples were also examined by x-ray diffraction techniques, and these results are summarized in Table 10. Except for high concentrations of noncrystalline phases such as amorphous silica, this technique in general detects only crystalline phases, and only those greater than approximately 5% in concentration.

The elemental concentrations listed in Table 9 and the compound identification provided by x-ray diffraction revealed some interesting features of these scale samples. The wellhead sample appeared to be ~88% PbS, 4% SiO₂, and a few percent of unidentified iron and calcium compounds. Silver,

probably as Ag₂S but possibly also as native silver, was present in an amount that made this material a valuable mineral.

The first-stage separated-brine scale, although formed at high temperature (200-220°C), appeared to contain ~27% SiO₂ and probably an equal amount of entrained NaCl. Although we have expressed the concentrations of silicon as SiO₂, we cannot rule out the possible presence of many metal silicate compounds as well. The only one actually identified was montmorillonite, a complex aluminum silicate (Table 10). The particular compound or compounds that yielded the high (22%) concentration of iron in this sample (or in the other scale samples as well) were not identified. In this

Table 10. Principal phases in scales from LLL four-stage flash system identified by x-ray diffraction.

Stage	Major phases	Minor phases
Wellhead	galena-PbS	amorphous silica-SiO ₂
1st-stage separated brine	amorphous silica-SiO ₂ halite-NaCl	calcite - CaCO ₃ galena-PbS montmorillonite clay
2nd-stage brine	amorphous silica-SiO ₂	halite - NaCl sylvite - KCl montmorillonite clay
2nd-stage steam	amorphous silica-SiO ₂	halite - NaCl
3rd-stage brine	amorphous silica - SiO ₂	halite - NaCl fluorite - CaF ₂ barite - BaSO ₄
3rd-stage steam	amorphous silica-SiO ₂	halite - NaCl fluorite - CaF ₂ sylvite - KCl
4th-stage brine	amorphous silica-SiO ₂ fluorite - CaF ₂	barite - BaSO ₄ halite - NaCl
Delay line	halite - NaCl amorphous silica-SiO ₂	fluorite - CaF ₂ barite - BaSO ₄ sylvite - KCl

sample, the iron may have arisen chiefly as a product of the corrosion of the pipe steel substrate, and many compounds were possible. It is interesting that this scale also contained calcite and montmorillonite clay, the former at a concentration of 5-10% if all of the calcium was present as CaCO₃.

The scales formed from the second- and third-stage brines appeared to be nearly two-thirds silica. Again, some metal silicates such as iron silicates also may have been present, but the elemental concentrations and the nonsiliceous compounds identified indicated that, as in many previous studies,¹ the dominant substance was amorphous silica. The third-stage brine scales and those formed downstream also exhibited significant concentrations of BaSO₄ and CaF₂ that, as discussed above, were also characteristic of the solids precipitated homogeneously from the system effluent brine. It may be more than a coincidence that these compounds first appeared at the point where the rate of growth of scale was a maximum.

The concentration of CaF₂ in scale formed at the fourth stage was strikingly high. Because of the high concentration of calcium and the evidence for CaF₂ obtained by x-ray diffraction, an additional analysis specifically for CaF₂ was carried out. A spectrographic method based on the observation of CaF molecular bands was used, and calibration was

based on National Bureau of Standards phosphate rock (3.92% F), opal glass (5.72% F), and pure CaF₂ (48.7% F). On the basis of this analysis, it was estimated that the concentration of CaF₂ in the scale from the fourth stage was 40%.

The scale found in the delay line apparently contained large amounts (~50%) of entrained NaCl. It also contained the highest concentration (~9%) of BaSO₄ and 10% CaF₂. A large portion of this scale might have been water soluble. The principal phases found in these low-temperature scales were also identified on the surfaces of mild steel exposed for much shorter periods of time to acidified brine²⁴; in those experiments, however, corrosion of the substrate also produced thin layers of elemental lead, PbCO₃, and copper-containing compounds. These compounds were evidently obscured in the bulk analysis of the thick long-term scales of the present study.

The trends in composition of the scales with temperature and location in the system illustrate the complex nature of the scaling processes in these geothermal systems. Because of the differing rates of the important reactions causing precipitation, both temperature and the "age" of the brine (with reference to its time of flow from the wellhead) are important variables in determining the distribution of compounds in the scales.

It is also apparent that approaches to scale control in these geothermal systems must take into consideration the variety of compounds that constitute the scales. A scale inhibitor that is effective throughout the fluid-handling structure will have to control metal-sulfide scales at high temperatures, amorphous silica (or silicates) at intermediate and low temperatures, and the crystalline phases such as BaSO₄ and CaF₂ at low temperatures. Moreover, agents that reduce the formation of these scale compounds would increase the exposure of the metal surfaces and hence their susceptibility to corrosion. Thus brine treatment to control scaling may also require special materials of construction or corrosion inhibitors. The ideal chemical additive for the control of scale and the protection of plant materials might be a mixture of compounds, each tailored to a specific task. On the other hand, it has long been believed^{25,26} that scales deposited from brines of the Salton Sea geothermal field are always formed on a silica substrate or in a silica matrix; thus it is possible that control of only a single compound, silica, will be the key to scale control in general.

The analytical results and interpretations reported here reveal several areas for future work that could enhance our understanding of the chemistry of these hypersaline brine systems. Although difficult in each case, more accurate and frequent measurements of the concentration of the scale-forming anions—sulfide, sulfate, and

fluoride—in the brine would be useful. A more detailed analysis of the scale and solids by techniques such as infrared spectroscopy, Raman spectroscopy, selective solvent leaching, microscopy, or even photoelectron spectroscopy might pinpoint their composition more precisely.

EFFECT OF ACIDIFICATION ON SCALING RATES

During most of the period of operation of the flash system, the brine was acidified by injection of hydrochloric acid. This afforded some comparisons of the acidified-brine scaling rates with those found for untreated brine. The flash system was operated for a total of 1042 h: 115 h without acid (pH of ~6.0) followed by 927 h with acid injection (pH of 4 to 5). Thicknesses of scale were measured by sectioning portions of the brine drain lines between stages. A summary of these observations is given in Table 11.

Comparison of the results for the 210°C line before and after acidification shows that the reduction in scaling rate due to the lowered pH was dramatic—a factor of about 21. An indication of the improvement in the scaling rates at the lower temperatures is possible by comparing the acidified-brine rates found here with rates for unmodified brine measured at the GLEF. The apparent decreases in scaling rates are factors of ~7.5, 2.6 and 8.3 at temperatures of 150, 125, and 105°C,

respectively. The lesser improvement at 125°C may have been due partly to the fact that, as shown below, the scales formed at this and lower temperatures begin to contain increasing amounts of BaSO_4 and CaF_2 . The precipitation of these substances, unlike that of SiO_2 , is not inhibited by the lowered pH. Another possible explanation for the peak in scaling rate at 125°C is that two effects tend to work in opposite directions. One is the degree in silica supersaturation, which increases as the temperature is lowered; the second is the rate of silica polymerization (or precipitation), which decreases (for a given degree of supersaturation) as the temperature is lowered. Thus the net rate of precipitation, or scaling, may reach a maximum at an intermediate temperature. Acid consumption and costs were found to be consistent with those reported previously for nozzle expansion tests.¹

Corrosion rates of carbon and low-alloy steels were generally increased^{2,7} by acidification of the brine to pH 4-5, and they are not considered

Table 11. Rates of scale formation in brine drain lines of LLL four-stage flash system.

Location	Scale thickness, mil	Time of exposure, h	Indicated scaling rate, mil/h	Scaling rate at GLEF, mil/h	Scaling-reduction factor ^a
1st-stage drain, 210°C (before acidification)	219	1042	0.21		
1st-stage drain, 210°C (after acidification)	31	1042 ^b	0.01		21
2nd-stage drain, 150°C	144	1042 ^b	0.08	0.6	7.5
3rd-stage drain, 125°C	187	532 ^c	0.35	0.9	2.6
4th-stage drain, 105°C	65	532 ^c	0.12	1.0	8.3

^aDecrease in scale deposition as pH lowered from 6 to 4-5.

^b115 h without acid; scaling rate calculated for acid period only.

^c2 h without acid; line cleaned before 532-h test period.

suitable as materials of construction for acidified brine service. Several materials suitable for application as liners on carbon steel vessels and piping were virtually unaffected after 927 hours exposure to brine at pH 4-5. These include Hastelloy C-276, Inconel 600, and 29-4 (29% Cr, 4% Mo, and 67% Fe). A complete report on the corrosion behavior of

a wide variety of materials exposed to acidified brine will be published as a companion paper⁷.

We are currently investigating other methods of scale control which do not involve reduction in pH, e.g., addition of organic polymers³ and sludge recycle. Such methods, if successful, may permit plant construction using the usual carbon steels.

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