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FINAL REPORT ON STUDIES OF BRINE CHEMISTRY
AND
SCALING AT THE SALTON SEA
GEOTHERMAL FIELD, 1977-1979

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FINAL REPORT ON STUDIES OF BRINE CHEMISTRY
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SCALING AT THE SALTON SEA GEOTHERMAL FIELD, 1977-1979

ABSTRACT

Summarized are the results of investigations of brine chemistry, the effects of brine acidification and organic additives on the rate of scale formation and scale composition, and the use of other additives for scale control. A bibliography of reports describing these studies is included. Recommendations are given for techniques and approaches for further testing of additives for silica scale control.

FOREWORD

The purpose of this report is to summarize the main features of the various studies related to brine chemistry and scaling that were carried out by the Lawrence Livermore National Laboratory (LLNL) at the Salton Sea Geothermal Field (Imperial Valley, California) during the years 1977 through 1979. It is intended as a partial sequel to the compendium edited by Austin, Lundberg, Owen, and Tardiff,¹ which described all of the activities of the LLNL Geothermal Program prior to 1977.

At the end of 1976, the organizations active in field studies of high-salinity, high-silica geothermal brines were LLNL, the San Diego Gas and Electric Company, the Imperial Magma Company, the U.S. Bureau of Mines, and the Union Oil Company. The first three of these organizations were commencing cooperative studies using the Magma Company's wells, particularly Magmamax No. 1 as a production well and Magmamax No. 3 as an injection well. At LLNL, Owen and coworkers^{1,2} had shown that the silica and sulfide scales formed from these brines could be virtually eliminated by lowering the pH of the brine, but the real severity of the scaling and corrosion problems were just beginning to be realized. Successfully conducting a meaningful test

without equipment malfunctions due to scaling or corrosion was itself a major accomplishment. On the basis of our early struggles with the test apparatus, the prospects of full-scale electrical power generation from these brines seemed to be remote.

However, by 1980, much progress had been made. Several technically (if not yet economically) viable chemical solutions to the scaling problem have been tested, several relatively low-cost metallic materials have been found that will resist the brine, a method for the treatment of spent brine for injection has been proven, many difficult chemical measurement techniques have been perfected, most of the environmental issues have been addressed, and the first increments of electrical power are now being generated.

During the 1977-1979 tests in the Imperial Valley, I was privileged to be associated with many very competent and congenial people, especially my colleagues at LLNL, whose names appear only in the references cited. Particular mention should be made of Frank Locke and John Grens of LLNL, and E. Kelly of Kelly Welding Services, who designed the brine handling equipment, kept it going for our experiments, and managed the test site. Several groups often were simultaneously performing experiments at Magmamax No. 1 well. We are indebted to Bill Jacobson of S.D.G.&E. and John Featherstone of Imperial Magma for facilitating our participation and making this such a smooth operation. Finally, I want to acknowledge George Tardiff and Larry Owen, LLNL Geothermal Program Leaders during this fruitful period, and Assistant Associate Director Fred Holzer, all of whom provided valuable technical direction, encouragement, and support.

ADDITIONAL TESTS OF BRINE ACIDIFICATION FOR THE CONTROL OF SCALE

It was shown by Owen and co-workers in a number of experiments reported previously^{1,2} that lowering the pH of the brine from its natural value of 5.5-6.0 with hydrochloric acid was effective in retarding the formation of scale from SSGF brine. A number of additional experiments were carried out to characterize this effect and to quantify the actual degree of scale reduction more accurately.

In the Fall of 1977, with the brine handling apparatus shown in Figure 1, we conducted experiments in which hydrochloric acid was injected into the brine at high temperature ($\sim 220^{\circ}\text{C}$) to control the pH of the effluent brine, and then the kinetics of the precipitation of silica and solids from the effluent brine at 90°C were measured as a function of pH.³ These measurements were made using a specially developed technique⁴ involving anaerobic incubation of the brine, filtration to determine the levels of suspended solids, and determination of the silica remaining in the filtrate (by atomic absorption spectrophotometry) as a measure of the dissolved silica. It was shown⁴ that this technique actually measures the silica existing in particles $< 1\ \mu\text{m}$ in size, thus it yields results somewhat higher than the concentrations of monomeric silica that would be measured by the silicomolybdate method.

Application of this technique to geothermal brine obtained from the four-stage flash system gave the results shown in Figure 2. Lowering the pH of the brine clearly retards the rate of silica precipitation, principally because the rate of silica polymerization is lowered,^{5,6} and this is the basis for control of scaling by brine acidification.

For the untreated and less acidic brines, the curves in Figure 2 suggest that equilibrium under these static conditions is reached after $\sim 100\ \text{h}$ incubation; however, subsequent studies⁷ revealed that 30 days are required for complete precipitation of the solids and for the silica to reach its equilibrium solubility. For this particular brine, the final values of the concentrations of silica and suspended solids (which were independent of the initial pH) were 191 mg/kg and 382 mg/kg, respectively. Note again that, because of the method of measurement, the former value is not the true solubility of monomeric silica.

Figure 1. Simplified schematic diagram of four-stage brine flash system.

Figure 2

EFFECT OF BRINE pH ON PRECIPITATION OF SILICA

90°C; Initial concentration of SiO₂-460 mg/kg; Brine chloride-3.7 M

During the winter of 1977 and 1978, a ~1000-h test was conducted with the four-stage system in which a variety of materials were exposed to determine their corrosion rates (see Reference 8). The specimens were "pre-scaled" by operation of the system with untreated brine for ~100 h, and then exposed for ~900 h to acidified brine with the pH controlled between 4 and 5. (About 300 ppm HCl in the brine was required.) This test was the only long term test of acidification, and it afforded a good measurement of its effect on scale formation. The results were compared⁷ with scaling rates of untreated brine measured at the Geothermal Loop Experimental Facility of the San Diego Gas and Electric Company, and the observed degrees of scaling-rate reduction due to acidification were as follows: at 210°C, 95%; 150°C, 87%; 125°C, 60%; and 105°C, 88%. For most of the test the brine salinity was in the range of 4.0 to 4.5 Mol/l chloride.

An interesting result of the 1000-h scaling and corrosion test was that the low-temperature scales were found to contain a significantly increased proportion of BaSO₄ compared to the scale formed from untreated brine, and CaF₂ was found for the first time. These compounds also appeared in the solids precipitated homogeneously from the brine during the incubation tests. The reason for the increased concentrations of these compounds was not established, but it is speculated that the increased BaSO₄ is due primarily to the known effect of acid in enhancing the rate of precipitation of BaSO₄. The formation of CaF₂ was not observed in subsequent experiments, thus higher fluoride concentrations may have been a transient condition of the well fluid. Later experiments always resulted in the precipitation of BaSO₄ when the brine was acidified.

Acidification of the brine also promotes the formation of certain other compounds during the early stages of the exposure of steel that is corroded by the geothermal brine.⁹ Lead carbonate (PbCO₃) was identified and probably arises because of neutralization of the acid during the corrosion process. Metallic lead and silver also are formed, probably because of either a replacement reaction with the dissolving iron, or a reduction of the soluble species of the metals at cathodic sites on the surface. Antimony and copper, in unidentified compounds, also are enriched in scale found on corroding surfaces. These various compounds are most prominent in thin

layers of scale formed during short-term exposures. The thickness of the scale layer at which surface reactions have negligible influence is not known. In any event, possible use of acidification for scale control in the future should take into account the concomitant changes in scale composition as well as scaling rate.

No long term tests were conducted to ascertain the degree of scale reduction as a function of the pH of the brine -- the only comprehensive data are those of the 1000-h test at a mean pH of 4.5. In the course of tests of organic additives for scale abatement,¹⁰ however, we obtained additional short term data on the effects of acidification to pH values of 5.0, 4.0, and 3.0 and there were some interesting results. Table 1 lists the rates of scale formation on three different materials found for untreated brine and brine at pH values of 5.0 and 3.0.

On the inert Teflon and Hastelloy surfaces, and at low temperature, reduction of brine pH has a dramatic effect. At pH 3.0, virtually no silica or heavy metal sulfide scale formed. There was also a very significant reduction in the amount of scale formed in the tubing exposed at 90°C. Chemical analysis showed that the small quantity of solids that formed on the mild steel specimens at pH 3 were corrosion products rather than "pure" scale formed solely from the constituents of the brine. In contrast, at pH 5.0 and 125°C, there was no decrease in the rate of scaling. This scale was silica and silica/metal-sulfide in composition, rather than corrosion product. Thus the formation of siliceous scale when the brine pH is lowered only slightly is probably due to the fact that corrosion of the steel neutralizes the acid in the vicinity of the metal and renders the brine heavily scaling again. Acidification to pH 3 overcomes this effect -- most of the Fe(II) corrosion product constantly dissolves away into the flowing brine, bare metal is constantly exposed, very little solid reaction product accumulates on the surface (except for some metallic Pb, Cu, Ag, and other more noble metal compounds), and silica precipitation remains suppressed by the high buffer capacity of the brine. The 1000-h test at a mean pH of 4.5 and incomplete short-term experiments at pH 4 indicate that the brine pH must be well below 4 to completely overcome the effect of the surface neutralization of the acid, and render the brine completely non-scaling. It is clear that corrosion of the substrate is not necessary for the adherence of scale, but it is an enhancing factor.

Table 1. Effect of acid on scaling rates of geothermal brine
(MagmaMax No. 1 Brine, 3.5-3.7 Mol/l Chloride; March, 1979 Test Series)

Brine pH	Time of Exposure h	Scaling Rate, mil/h						
		Coupon, 210°C			Coupon, 125°C			Tubing 90°C
		Mild Steel	Hastelloy	Teflon	Mild Steel	Hastelloy	Teflon	Mild Steel
5.8 (Untreated)	88	0.05	0.02	0.02	0.10	0.03	0.04	1.2
5.0	68	0.13	<0.01	<0.01	0.15	<0.01	<0.01	0.1
3.0	69	0.08	<0.01	<0.01	0.03	<0.01	<0.01	0.05

Acidification to pH 3, however, significantly increases the rates of corrosion of steel in hypersaline geothermal brine. Not only is the surface not protected by silica scale, but the inherent corrosion rate of mild steel in high chloride solutions increases sharply below pH 4.¹¹ Using the linear polarization resistance technique,^{12,13} we measured corrosion rates at pH 3.0 of 40 mpy at 210°C and 120 mpy at 125°C.¹⁰ Thus it appears that with acid alone, the price paid for complete scale abatement would be rather high corrosion rates for mild steels. A better approach, as outlined in more detail below, is probably a combination of acid and an organic compound that functions as both silica precipitation inhibitor and a corrosion inhibitor. Both scaling and corrosion could then be minimized. Of course, selection of resistant materials would also be important, but the work of McCright et al.⁸ has shown that there are some low-alloy, relatively low cost steels that are much more resistant to the brines than mild steels.

STUDIES OF BRINE CHEMISTRY AND ITS EFFECT ON SCALING

Chemical analyses and testing of additives during the many periods of Magmamax No. 1 well operation from 1977-1979 revealed that the levels of dissolved salts and probably also some of the volatile components varied considerably with the history and flow rate of the well. The effluent brine, i.e., brine flashed to atmospheric pressure and a temperature of 105°C (through two to four stages) was routinely monitored by measuring its pH, density at 25°C, chloride concentration, and silica concentration. The density, chloride concentration, and to a lesser extent, the silica concentration, always increased with increased well flow rate. For example, a change in total well flow rate from 50 to 500 gpm typically resulted in a change in chloride concentration from 3.5 to 4.5 Mol/l.⁷ The concentrations of the dissolved metallic constituents of the brine (e.g., the alkali and transition elements) followed the salinity, and there was evidence that the levels of H₂S in the steam increased with well flow rate. The work-over history of the well also influenced the brine salinity at a given flow rate, and in one instance the salinity was permanently altered by a local earthquake.¹⁰

In the course of our studies we examined the brine from three wells in the Salton Sea Geothermal Field: Magmamax No. 1, with which most of our work was done, Magmamax No. 2, and Woolsey No. 1. Table 2 compares some of the characteristics of these brines. Samples were taken when the total well flows were at least 500 gpm.

Magmamax No. 1 and Woolsey No. 1 brines were quite similar in composition except for a significantly higher concentration of sulfate in the Woolsey brine. In incubation tests of the effluent Woolsey brine,¹⁴ the higher sulfate led to the precipitation of large amounts of BaSO_4 after an induction period of ~10 h. The suspended solids level for this brine eventually reached 550 mg/kg. However, because of the delay in the precipitation of BaSO_4 from the Woolsey brine, the concentration of BaSO_4 in the low temperature scale formed from this brine at the GLEF still was not large. The concentration of BaSO_4 in the low temperature scale was 0.5% after Magmamax No. 1 operation and only 1.0% after operation

Table 2. Principal features of the composition of geothermal brines at the Salton Sea Geothermal Field.
(Effluent brine flashed to atmospheric pressure)

	Magmamax No. 1	Magmamax No. 2	Woolsey No. 1
Date Sampled	Jan., 1978	May, 1978	Feb., 1979
Density at 25°C, g/cm ³	1.171	1.193	1.166
Chloride, Mol/l	4.46	4.91	4.13
SiO ₂ , mg/kg	548	see text	510
Fe, mg/kg	233	780	215
Sulfate, mg/kg	41	not determined	108

with Woolsey No. 1.¹⁵ Thus, even though high levels of sulfate in these brines represents an unstable condition, the precipitation of BaSO_4 will not be an important factor in scale formation unless, as described above, it is accelerated by lowering the pH of the brine.⁷ It is interesting to note that the origin of the sulfate in these brines has never been satisfactorily explained.

Magmamax No. 2 brine was distinctly more saline than either Magmamax No. 1 or Woolsey No. 1, being more akin to the brine of Sinclair No. 4 investigated previously.¹ Magmamax No. 2 brine also was much higher in iron (see Table 2), but not silica, than Woolsey or Magmamax No. 1 brines. The rate of precipitation of solids and silica from Magmamax No. 2 brine was much higher -- the level of suspended solids in prompt samples after the atmospheric flash already was 170 mg/kg. The sum of the suspended solids and dissolved silica values indicated that the initial dissolved silica was ~550 mg/kg, like that of the other two wells.

Part of the reason for the more rapid precipitation of silica from the Magmamax No. 2 brine probably is the high concentration of iron. As the brine flashes and its pH rises, Fe(II) species hydrolyze and can aid in the nucleation of the silica.^{6,16} Another reason is the increased salinity, which lowers the equilibrium solubility of silica.⁷ It was found⁷ that at 90°C, the "solubility" of silica (as SiO_2) decreased from 184 mg/kg at 3.5 Mol/l chloride to 140 mg/kg at 4.9 Mol/l chloride. At a given initial concentration of silica at the wellhead, the higher salinity means a higher degree of supersaturation as the brine is cooled, and thus a higher rate of precipitation and scaling.

Figure 3 illustrates how the scaling rate at 125°C varied with brine salinity and with the type of scaling surface. Scaling rates at 220°C and 125°C were measured using three different materials to provide an indication of the effect of substrate corrosion on scaling rates. In contrast to mild steel, neither Teflon TFE nor Hastelloy C-276¹³ is attacked appreciably by the hypersaline brine. As can be seen in Figure 3, scale accumulates at a lower overall rate on the inert surfaces, either because of a lack of corrosion product on which to adhere, or because of the absence of the chemical reactions of corrosion that tend to induce scaling. This effect, however, may not persist at longer exposure times as the scale becomes thicker.

Figure 3

EFFECT OF BRINE SALINITY ON SCALING RATE AT 125°C

MagmaMax No. 1 Brine; ~ 500 mg/kg SiO₂

The variation in scaling rate with brine salinity required that the experiments on methods of brine treatments to reduce scaling be designed so that results could be compared on an equal salinity basis. As mentioned above, a higher salinity decreases the equilibrium solubility of silica and its supersaturation, thus this decreases the effectiveness of a given additive in reducing the rates of precipitation and scaling.¹⁰

The scales formed on the test coupons during the scale abatement studies were extensively analyzed and provided additional information on the characteristics of these deposits. Table 3 summarizes the elemental analyses of several types of deposits, and illustrates how the composition of the deposit changes with location (temperature) in the geothermal system and substrate material. As noted elsewhere, corrosion of the mild steel introduced constituents into the scale that are not found in deposits formed on inert surfaces (cf. 125°C). We also found that after steam separation, at high temperature (the 220°C data in Table 3) the proportion of silica in the scale increased from ~4 to ~60%. Thus, confirming previous modeling studies,¹ loss of the volatiles from the brine and the subsequent pH rise, even under essentially isothermal conditions, causes a profound change in the nature of the scale. Then, as the temperature decreases further in the geothermal system, the scale increases further in the proportion of silica.

TABLE 3. ELEMENTAL ANALYSES OF SCALES FORMED ON TEST SPECIMENS BY UNTREATED BRINE.
(MagmaMax No. 1 Brine; 4.0 mol/l Chloride; 113 h Exposure; 0.3-0.6 mm scale thickness)

Element	Concentration, Wt. %				
	220°C	125°C			90°C
	TFE	TFE	Hastelloy	Mild steel	Mild steel
	Teflon	Teflon	C-276	(AISI 1009)	
	Coupon	Coupon	Coupon	Coupon	Tubing
Si as SiO ₂	57	83	81	66	63
Na	0.6	n.d. ^a	0.5	0.6	6.9
K	0.2	0.8	1.0	0.7	1.0
Ca	1.8	0.45	0.45	0.75	2.7
B	n.d.	n.d.	0.06	0.6	n.d.
Al	0.5	n.d.	n.d.	1.9	0.1
S	0.5	0.3	0.44	1.1	n.d.
As	<0.1	0.03	<0.01	0.53	<0.03
Sb	<0.1	<0.02	0.02	2.8	n.d.
Fe	21	1.1	1.0	2.3	0.15
Mn	1.3	0.20	0.17	0.20	0.17
Cu	0.3	0.59	0.31	6.0	0.03
Pb	4.0	0.21	1.6	0.91	0.6
Ag	0.04	0.03	0.04	0.18	n.d.
Cl	0.2	0.08	<0.02	0.2	2.7

^a Not determined

TESTS OF ALTERNATIVE METHODS OF BRINE TREATMENT FOR SCALE CONTROL

Introduction

The success of brine acidification to control scale has been tempered by several disadvantages of the technique. First, the large quantity of HCl required (~ 300 ppm in the brine to reach pH 5) would represent a significant fraction of the cost of power generated. Second, the pH of the brine must be lowered from ~ 6 to ~ 3 for complete scale control, and this significantly increases corrosion rates. As noted above, prevention of formation of the siliceous scale, by itself, tends to increase corrosion rates; moreover, below a pH of about 4, the inherent rate of corrosion of steel in highly-saline brine increases sharply.¹¹ Finally, it appears that sludge-bed reactor clarification will be used for the treatment of brine effluents prior to injection,^{17,18} and brine acidification would interfere with this process.

Thus in 1978 we turned our attention to an investigation of alternative chemical methods of brine treatment to control scale, and we concentrated primarily on determining the feasibility of using organic compounds for this purpose. Several other chemical approaches and the technique of seeding were also briefly tested. For these studies, the brine flashing equipment was configured as a three-stage, dual-channel system, specifically designed to characterize scaling rates at three temperatures: ~ 220 , 125, and 90°C .

Brine Scaling and Corrosion Measurement Apparatus

Several types of specimens and test equipment were used to measure the scaling and corrosion characteristics of the brine. The locations of these specimens are shown in the schematic diagram of the brine treatment test system in Figure 4 and are as follows:

1. Pipe Spools. These were 24-in.-long sections of 1-in.-i.d. mild steel pipe which were installed in the 220 and 125°C drain lines of the system. After use, the pipe section was potted with epoxy, cut in cross section, and polished for measurement of the accumulated scale.

Figure 4. Simplified Schematic diagram of the brine treatment test system.

2. Mild Steel Coupons. These were 1.25 x 0.5 x 0.025-in. coupons of AISI 1009 steel. In early work, these coupons were mounted on a holder as shown in Figure 5. These holders were mounted in the downstream flanges of the pipe spools. In later work, because some plugging caused by this arrangement occurred, the steel coupons were mounted on 2-in. pipe plugs installed in the 2-in. lines next to the Petrolite probes. The weight gain and thickness increase (as measured by a micrometer or metallographically) were determined after exposure to provide an indication of the combined effects of corrosion and scaling.

3. Petrolite Corrosion Probes. These were type 510 three-electrode probes fitted with AISI 1018 mild steel electrodes, for estimation of corrosion rates by the linear polarization resistance (LPR) technique.^{12,13} The probes were connected to Petrolite Model M-3010 automatic recording instruments for continuous monitoring of the corrosion rates.

4. Inert Test Coupons. These were designed, as described above, to measure the purely scaling tendency of the brine, apart from the effects of corrosion. These coupons were 1-1/4 x 5/16 x 0.1-in. pieces of TFE Teflon and Hastelloy C-276 and were mounted on the Petrolite corrosion probe assemblies as shown in Figure 6.

5. Stainless-Steel Screens. These were 47-mm diameter disks perforated with 0.4-mm holes, and were contained in Millipore high-pressure filter holders. Screens were installed in sidestreams from the 220°C brine lines and at the 125°C sample ports. The screens were intended to provide a qualitative or semiquantitative measurement of the brine scaling tendency; unlike the other test specimens, they were removable during the course of an extended run. The scaling tendency of the brine was indicated by the visual appearance and weight gain of the screens during exposure.

6. Tubing Specimens. These consisted of short sections of 0.25- and 0.50-in.-diam. mild steel tubing, which were attached to the output of the delay stage. Flow through the tubing was regulated with an output valve and the rate was adjusted to maintain a delay of ~10 min. from the 125°C flash point and a temperature at the specimen of ~90°C. For examination, the specimens were handled in the same manner as the pipe spools.

Figure 5. Steel coupon assembly for measurement of scaling and corrosion in geothermal brine.

Unexposed

Figure 6. Petrolite probe with coupons for measurement of scaling and corrosion in geothermal brine.

A major emphasis in our work was to develop and use techniques of scaling rate measurement that would minimize the time required to evaluate a single additive, but still provide useful information for prediction of performance in larger facilities and for longer times. Use of the 1-inch-i.d. pipe spools appeared to be a reliable semi-quantitative indicator of brine scaling tendency. However, at least 60-h exposures were required when these specimens were used. Another disadvantage was the wide variation of scale thickness in a given exposed specimen. In one cross-section, the typical range was a factor of 2 to 4. Longer exposure times would have tended to smooth out this variation. The most precise and convenient-to-handle indicators of scaling at 220 and 125°C were the coupons of mild steel and inert material. Using these specimens for at least 40-hr exposures, it was estimated that the overall uncertainty in scaling rate measurement was $\pm 40\%$ at 220°C and $\pm 25\%$ at 125°C. At 90°C, where scaling rates approached 0.2-in./day, the tubing sections also gave results precise to $\pm 25\%$. Because the screens were very sensitive to the particulate level in the brine, they did not always provide a reliable indication of the "true" scaling tendency of the brine.

The Petrolite LPR equipment was always used in the anodic polarization mode to avoid possible errors due to electrodeposition of brine constituents such as Pb^{2+} . This equipment performed reliably and gave a very useful semiquantitative, real-time indication of the effects of both corrosion and scaling. Scaling was always evidenced by rapidly decreasing readings, and the lack of scaling, such as during brine acidification runs, was also apparent from the high corrosion rates. The LPR data also suggested that certain organic additives acted as corrosion inhibitors.

Tests of Proprietary Chemical Additives^{14,19}

In the Fall of 1978, an industry solicitation was conducted in which the leading water-treatment companies were contacted and asked to submit compounds for tests as antiscalants. Eight additives from eight different companies were evaluated later that year at temperatures of 220 and 125°C. In the Spring of 1979 an additional type of brine treatment was examined, the Austral-Erwin process, in which an oil emulsion is injected into the brine. In addition to scaling rate measurements, the effects of the additives on the rate of precipitation of silica from the effluent brine and the chemical composition of the scales was determined. We concluded¹⁴ that none of these

brine treatments had a very beneficial effect on the rates of scaling from the brine of Magmamax No. 1 well. Among the chemical additives, Southwest Specialty Chemical's SC-210 showed marginal promise, and a modification of the method of addition of the Austral-Erwin additive might be more effective than the one we tested. Its principal effect was in altering the consistency and adherence of the scale. A difficulty, to be discussed in more detail below, was that the oil emulsion apparently rendered the suspended particles of silica hydrophobic.

Most of the chemical additives in the original eight were of the phosphonate type found in many other applications to be effective against crystalline scales such as CaCO_3 and CaSO_4 . They were really not expected to be very effective against the amorphous silica, and indeed we found no effect on the precipitation rate of silica at 90°C . However, some of the proprietary phosphonates did diminish the silica scaling rate at 125°C slightly (20-50%), and we later found¹⁰ that a phosphonate in combination with a silica precipitation inhibitor enhanced its overall antiscalant activity. We attribute this to the hypothesis of Rothbaum et al¹⁶ and Owen⁶ that nucleation of particles of CaCO_3 (which would be inhibited by the phosphonate) are in turn responsible for some of the deposition of silica. There is evidence also that nucleation of hydrated iron oxides enhance the precipitation and deposition of silica.

In the course of the subsequent generic chemical testing, eight additional proprietary additives were subjected to the silica precipitation kinetics test, but none showed promise.¹⁴ In general, most of the substances used in the water treatment industry as antiscalants, and those which we tested as proprietary additives, appear to be compounds that are anionic in character. In contrast, our later generic chemical testing revealed clearly that cationic compounds, as a class, are the most effective in inhibiting silica precipitation and scaling.

Tests of Generic Chemical Compounds

The first tests of generic chemical compounds, i.e., compounds whose chemical identity was known to us, were carried out during the winter of 1977-1978. In those tests, which were performed concomitantly with the corrosion tests in acidified brine, a broad spectrum of compounds were added to samples of the brine off-line, and then their effect on the kinetics of precipitation of silica at 90°C were observed. These tests revealed²⁰

that many compounds containing the ethylene oxide moiety, $-\text{CH}_2-\text{CH}_2-\text{O}-$, were effective in stabilizing colloidal silica in geothermal brine. In subsequent on-line scaling tests, in which candidate additives were injected into flowing brine at wellhead temperatures,^{19,21} one such ethoxylated compound, a hydroxyethylcellulose, emerged as the most powerful inhibitor of silica precipitation at 90°C ; but it failed to retard the formation of geothermal scales at test temperatures of 210°C and 125°C .¹⁹

These initial results were sufficiently promising, however, to warrant continued testing of organic compounds, so we embarked on a series of systematic tests in which, ultimately, over 120 compounds were examined in Magmax No. 1 (primarily) and Woolsey No. 1 brines. It was assumed in testing these substances that a prerequisite for antiscalant activity was the ability to inhibit the precipitation of silica, at least at 90°C . Thus our procedure was to screen compounds first by injection into the brine at high temperature, sample the effluent brine at 105°C , and then measure the kinetics of silica precipitation in containers incubated at 90°C . The details of this technique are described in more detail below and in Reference 4. This technique enabled testing one additive at one concentration every 2-3 hours in each channel of the brine treatment system and conserved valuable field testing time. This method of evaluation also established the ability of the candidate compounds to survive the flashing high-temperature, high-flow, high-ionic strength conditions of the brine, which also is a prerequisite for an effective antiscalant.

Initially, sources such as that of Iler²² were used as guides for the selection of compounds that might interact with the colloidal silica in the brine. As noted, it became apparent early in our testing that compounds containing the oxyethylene moiety were especially active. In addition, cationic-functioning compounds such as quarternary ammonium compounds and polymeric amines also appeared to be an effective group of inhibitors. Table 4 lists, in approximate decreasing order of activity, the classes and examples of compounds that were found to inhibit the precipitation of silica.^{10,23-26} An example of precipitation kinetics data for one of these compounds, PAE·HCl, is shown in Figure 7. The brine composition is not identical, but comparison of the data of Figure 7 with that of Figure 2 shows that the addition of 20 ppm of PAE·HCl is equivalent to acidification to a pH of approximately 5.

TABLE 4. CLASSES AND EXAMPLES OF COMPOUNDS THAT STABILIZE COLLOIDAL SILICA IN HYPERSALINE GEOTHERMAL BRINE

<u>Class</u>	<u>Compound Trade Name</u>	<u>Chemical Name^a</u>	<u>Manufacturer</u>
Polyethylene Imines	Corcat P-18	Polyethylene imine, M.W. $\approx$ 1800	Cordova Chemical
Polyamines	PAE-HCl	Poly(aminoethylene, HCl) M.W. $\approx$ 120,000	Dynapol
Quaternary Ammonium Compounds: Polymeric	Mirapol A-15	(a polydiquaternary)	Miranol Chemical
Ethoxylated	Ethoquad 18/25 or Q-18-15	Methyl polyoxyethylene(15) octadecylammonium chloride	Armak or Tomah Products
Non-ethoxylated	Hyamine 1622	Di-isobutyl-phenoxyethoxyethyl dimethylbenzlammonium chloride	Rohm and Haas
Polyoxyethylene Polymers	Carbowax 14,000	Polyoxyethylene, M.W. $\approx$ 14,000	Union Carbide
Polyoxyethylene Alkylamines	Ethomeen 18/25	Polyoxyethylene(15) octadecylamine	Armak
Hydroxyethylcelluloses	Natrosol 250LR	Hydroxyethylcellulose, M.W. $\approx$ 85,000	Hercules
Polyoxyethylene Esters of Fatty Acids	Lipal 200C	Polyoxyethylene(200) ricinoleic acid triglyceride	PVO Int'l
Polyoxyalkylene Copolymers	Pluronic F38	Polyoxyethylene-Polyoxypropylene block copolymer, M.W. $\approx$ 5000	BASF-Wyandotte
Polyoxyethylene Alkyl phenols	Conco NI-125	Polyoxyethylene(200) nonylphenol	Continental
Polyethyloxazalines	XD-8779.00	Polyethyloxazaline, M.W. $\approx$ 60,000	Dow Chemical

^aNumber in parentheses denotes the number of molecules of oxyethylene per molecule of compound

Figure 7. Inhibition of precipitation of solids and silica from geothermal brine by an organic additive, PAE·HCl. 20 ppm additive; incubation of 90°C.

Within each compound class, large differences in activity among compounds were found, depending on such features as molecular weight, molecular structure, and the amount of oxyethylene. To the extent possible, an attempt was made to find the optimum compound within each class; for example, in the homologous series of polyoxyethylenes (Carbowax and Polyox compounds), with molecular weights ranging from 350 to 200,000, it was found that 14,000 was the most active.²³ As shown in Table 4, a much lower molecular weight polyethylene imine and a much higher molecular weight PAE·HCl (and other polyamines) appeared to be optimum in these classes. These differences are evidently related to the nature of adsorption of these compounds on the particles of colloidal silica. Comparisons of the best particular compounds within each class showed that the nitrogen-containing compounds were about equal as precipitation inhibitors, followed by the polyoxyethylenes and polyoxyethylene alkylamines together in an intermediate group, with the other classes listed in Table 4 in a lower activity group.

Classes of compounds that apparently did not react with silica in the geothermal brine were the following: polyacrylates, polymaleic acid, sulfonates, lignosulfonates, phosphate esters, phosphonates, non-ethoxylated cellulose derivatives, technical proteins, and silanes. It is also possible that some of these compounds thermally decomposed or hydrolyzed before they could react with the silica. Because many of these compounds are anionic, and because activity toward silica was exhibited by many cationic substances, it appears that electrostatic attraction or repulsion involving the negatively-charged colloidal silica is an important factor in the interaction. Most of the ethoxylated compounds are nonionic; their interaction with the silica probably involves the formation of hydrogen bonds.²²

Several compounds tested, which contained functional groups known from these and other studies²² to interact with colloidal silica, had the effect of slightly enhancing the rate of silica precipitation. Indeed, it is notable that many of the compounds and types of compounds that we have found to be good inhibitors are used in other applications as flocculants for silica. The exact mode of behavior of a particular compound clearly depends on a number of factors, among which are the relative concentrations of additive and colloidal silica, and probably the sizes of the particles of colloidal silica when

interaction with the additive occurs. It is well known²² in studies of the flocculation of colloids by means of a bridging agent that a rather critical concentration is required; an increase in the concentration of the additive may completely cover the particles, redisperse them, and in effect cause the additive to become a stabilizing agent.

Several of the most promising precipitation inhibitors (see Table 4) and various combinations of these substances with other compounds were evaluated to determine their effects on the scaling tendency of the hypersaline brine. At the highest temperatures, 210-220°C, no organic compound was found that unequivocally reduced the rate of scale formation; lowering the pH of the brine remains as the only effective treatment at this temperature. At the lowest temperature, ~90°C, we found that all of the individual compounds that decreased the rate of precipitation of silica in the static tests also reduced the rate of scale formation -- some, as will be described, to a significant degree. Two compounds, Corcat P-18 and PAE·HCl, also clearly retarded the scale formed at 125°C, but this intermediate temperature appears to be a point at which the scale is especially difficult to control.⁷ Here the driving forces for silica precipitation -- the degree of supersaturation and the temperature -- are both high.²⁷

Several substances that significantly retarded the low temperature scales had the effect of increasing the rate of scaling at 125°C. These included Carbowax 14,000, two polyoxyethylene alkylamines, and several proprietary additives.¹⁴ This behavior and that of the more successful compounds provide further clues as to the mechanism of the inhibitor action of these compounds, and in general seems to bear out the expectations from colloid theory. Inhibition of precipitation of silica appears to occur by the mechanism of steric stabilization.²⁸

In ideal steric stabilization,²⁸ the stabilizing molecules anchor themselves to the particles in such a way that the particles are covered with a diffuse layer that is compatible with, or soluble in, the dispersion medium. The absorbed molecules act as a barrier to retard the contact and aggregation of the particles. Figure 8 illustrates this process schematically. Strongly anchoring functional groups, which either adsorb or react, are necessary to withstand the dislodgment forces of Brownian motion

Figure 8

STERIC STABILIZATION OF SILICA COLLOID

and fluid shear. The nature of the solubilizing moiety of the stabilizing molecule is also important. It appears from our work that the solubilizing moiety must be strongly hydrophilic to keep the silica particles dispersed in the high-temperature, highly-saline brine. Additives that render the particles surfaces hydrophobic probably promote aggregation by "hydrophobic bonding."²⁹ This process involves the adsorption of the agent on the surface, oriented so that external hydrophobic areas are produced; these areas on different particles then unite and the particles are held together by the surface tension forces around the negative radius of curvature at the zone of contact. The polyoxyethylene homopolymers may have a propensity to act in this manner because of their inverse solubility/temperature behavior. Thus, while quite soluble and good scale inhibitors at 90°C, they tend to become insoluble and fail as inhibitors at higher temperatures.

Compared to the polyoxyethylene homopolymers and derivatives, the nitrogen-based compounds performed better as antiscalants, probably for several reasons: (1) they do not tend to become insoluble at high temperatures; (2) in the case of the nitrogen-containing homopolymers, the entire molecule is hydrophilic; and (3) electrostatic attraction between the cationic additive and the negatively charged silica particle results in a stronger bond. Table 5 summarizes the data obtained for several of these substances in tests conducted at two different levels of brine salinity.

The best single compound was Corcat P-18, which reduced the rate of formation of the 90 and 125°C scales by factors of ~18 and ~4, respectively. Figure 9 is a photograph of cross sections of tubing exposed to both untreated and Corcat-treated brines. Corcat P-18 is the lowest molecular weight (~1800) version of the series of polyethylene imines that were tested. It has the structure:

TABLE 5. EFFECT OF ORGANIC ADDITIVES ON SCALING RATES OF HYPERSALINE GEOTHERMAL BRINE (Magmamax No. 1 Well; mild steel specimens)

Additive	Scaling Rate, mm/day				
	210-220°C		125°C		90°C
	Steel	Teflon	Steel	Teflon	Steel
	Brine Chloride = 4.1 Mol/l, 40 hour tests				
Control; no additive	0.02	0.02	0.12	0.12	3.9
Corcat P-18 (35 ppm)	0.02	0.02	0.03	0.035	0.22
PAE-HCl (35 ppm)	0.006	0.005	0.05	0.055	0.5
Ethoquad 18/25 (35 ppm)	0.006	0.01	0.18	0.36	0.9
Ethoquad 18/25 (27 ppm)	0	0.005	0.05	0.012	1.0
+					
HCl (100 ppm)					
Brine Chloride = 4.5 Mol/l, 66-69 hour tests					
Control; no additive	0.06	0.04	0.48	0.41	3.0
Ethoquad 18/25 (25 ppm)	0.25 ^a	0.08	0.41	0.31	1.7
Ethoquad 18/25 (20 ppm)	0.09	0.06	0.27	0.32	0.55
+					
Dequest 2060 (5 ppm)					

^a System upset caused excessive scaling

Figure 9

EFFECT OF CORCAT P-18 ON GEOTHERMAL SCALE AT 90°C

Untreated brine
7 h

35 ppm Corcat P-18
21.5 h

Corcat P-18 and polyethylene imines, in general, appear to have the further advantage of being corrosion inhibitors for iron. These substances have been used as inhibitors in pickling baths,³⁰ and our experiments also indicated corrosion inhibitor activity in the hypersaline geothermal brine. Measurements by means of the linear polarization resistance technique^{12,13} showed a corrosion rate for mild steel at 125°C in the presence of 35 ppm Corcat P-18 of ~0.03 mm/yr (1.2 mpy), compared to ~1.3 mm/yr (5 mpy) for untreated brine.²⁶ Not only is the corrosion inhibition beneficial per se, but it probably contributes to the efficacy of the substance as a silica scale inhibitor by affecting the adherence of the scale.

As shown in Table 5, PAE·HCl was not quite as good an antiscalant as Corcat P-18, but it alone reduced the scale formed at 220°C. However, this effect was probably due to the presence of hydrochloric acid in the additive solution. The structure of this compound is,

where $n \approx 2700$, and it is an essentially linear polymer.

The results obtained for Ethoquad 18/25 as an antiscalant were mixed. In the precipitation inhibition tests, this compound and the similar trimethyloctadecylammonium chloride (Armak Arquad 18/50) were the best inhibitors in their homologous series and were equal to Corcat P-18 and PAE·HCl. As shown in Table 5, the coupon thickness measurements for 220°C in the weaker brine (4.1 Mol/l chloride) indicated that Ethoquad reduced the scaling rate, but this was probably in error because it was not verified by the coupon weight changes. At 90°C there was a good reduction in scaling rate (less satisfactory in the stronger brine, as expected). At 125°C in the stronger brine, Ethoquad had very little effect on the scaling; in contrast, at a higher concentration in the weaker brine, at 125°C, it had the detrimental effect of increasing the scaling rate. The concentration of Ethoquad used in the weaker brine probably represented a condition of overfeeding¹⁰; because Ethoquad is a surfactant, the enhanced deposition of scale, as discussed above, may have been due to the phenomenon of hydrophobic bonding.

Several combinations of two compounds were evaluated as antiscalants and the results of two such combinations are also listed in Table 5. The mixture of Ethoquad 18/25 and Dequest 2060 (Monsanto diethylenetriamine pentamethylene phosphonic acid) is better than the Ethoquad alone, especially at 90°C. As noted above, the action of the phosphonate here may be to inhibit CaCO₃ precipitation, thus indirectly and partially retarding silica nucleation.

The results of the test of the combination of Ethoquad 18/25 and hydrochloric acid (shown in Table 5) are especially interesting because an amount of acid was used that did not greatly change the pH of the brine. The pH change (of the effluent brine) was only from 5.95 to 5.75, yet, compared to Ethoquad alone, there was a marked decrease in the rate of precipitation of silica in the static test at 90°C, and a significant reduction in the scaling rates at 220 and 125°C. The lack of an additional effect of acid on the scaling rate at 90°C, compared to Ethoquad alone, is attributed to an increased corrosion of the specimen which compensated for the decreased rate of silica deposition. The effect of the combination of acid and silica inhibitor is probably synergistic: high temperature injection of the acid should retard silica particle growth and allow adsorption of the organic compound at an earlier stage in the process of growth. There is evidence that, for effective steric stabilization of the colloidal silica to occur, the particles must interact with the inhibitor when their sizes are of the order of 0.1 μm.

The use of an organic silica-precipitation inhibitor together with a small amount of hydrochloric acid appears to be the optimum way to realize the benefit of both compounds. This is important because of the relatively high cost of the organic additives. Assuming that the basic cost of power generation at the SSGF is 33 mill/kWh and that 100 kg of brine would yield 2.2 kWh,³¹ then at a concentration of 20 ppm and \$2.00/kg the additive would represent ~6% of the cost of power generation. Most of the organic compounds that we have tested are more expensive: Corcat P-18, for example, is ~\$13.00/kg. A total cost advantage could be gained by trading off a quantity of organic compound for the much less expensive hydrochloric acid (~\$0.25/kg) in the final formulation, and the mixture could be optimized with respect to concentration in the brine, the degree of scale inhibition, and tolerable

corrosion rates. Since periodic cleaning of geothermal facilities will be required, the ultimate benefit of a particular scale control technique will be measured by the frequency and ease of plant cleaning (or plant availability). The silica precipitation inhibitors have the additional benefit of rendering the low temperature scales easier to remove. Because costs of the various options are changing rapidly, cost analyses such as these will have to be done carefully for each specific geothermal system design.

Conclusions and Recommendations for Future Studies of Organic Additives

Based on the results of the scaling tests and the various criteria established for a chemical additive for hypersaline geothermal brine,¹⁰ we believe that Corcat P-18 is the most promising single compound at the present time. It reduces the rate of scale formation at low and intermediate temperatures, is also a corrosion inhibitor, has a relatively low molecular weight, and has good physical properties (high activity, non-foaming liquid). Its high cost could be mitigated, and overall performance enhanced, by combination with hydrochloric acid. A second choice of silica dispersant would be PAE·HCl, followed by the less satisfactory Ethoquad 18/25. A ternary mixture consisting of a silica precipitation inhibitor, acid, and a phosphonate, crystalline-scale inhibitor such as Dequest 2060, would probably be best of all.

Additional experiments with such combinations, and tests of other silica precipitation inhibitors, obviously should be performed, but were precluded in our study by limitations on the field testing time. Among other compounds that were only partially evaluated, the most promising are Mirapol A-15 and Hyamine 1622 (see Table 4), Armaq Arquad 18/50, and American Cyanamid Cyfloc (a polymeric tertiary amine). The type of compound that has emerged as a potent silica precipitation inhibitor suggests that a number of similar polymeric nitrogen compounds that are used in the water treatment industry as flocculants should also be investigated as silica inhibitors for geothermal systems. These compounds are less expensive than the ones we tested.

Tests of Other Methods of Scale Control

Several other approaches to scale control were briefly investigated. The experiments were designed only to test the feasibility of the techniques and reveal problems, rather than to be thorough evaluations.

One of these techniques was the addition of silica sludge to the brine as a method of seeding to accelerate the rate of silica precipitation.^{14,19} The rationale was simply that if the dissolved silica deposited on the seed particles in preference to the brine handling equipment, a degree of scale abatement could be achieved. Sludge seeding had already been shown to be a successful method for the treatment of effluent brines for injection.^{17,18} Our preliminary experiments¹⁹ demonstrated that seeding with sludge particles from a reactor/clarifier (mean particle size $\sim 10 \mu\text{m}$) did indeed lower the levels of dissolved silica in the brine, which should reduce scaling rates, but the degree of scale abatement could not be assessed. Our brine handling system and scaling-rate measurement techniques were not suitable for long-term tests with the high levels of suspended solids in the seeded brine. However, subsequent tests of this concept by the Imperial Magma Company have appeared promising.³² Seeding with synthetic colloidal silica particles with diameters below $1 \mu\text{m}$ also would be worth evaluation, if this material could be introduced into the brine without coagulation.

A similar problem of coagulation due to the effect of locally high concentrations of the injected additives arises with the injection of alkali into the brine. This was attempted on two occasions, once when NaOH was injected to ascertain the effect of increasing the pH of the brine on the concentrations of monomeric silica,¹⁰ and later as an experiment in which an inhibitor was combined with NH_4OH for injection.²⁶ Ammonium hydroxide injection had been proposed as a chemical treatment for scale control in a patent,³³ and appears to have some merit if silica particle size can be controlled and/or flocculation of the particles prevented. However, high suspended solids levels would have to be tolerated as in seeding. In addition, we found that, to prevent excessive scaling due to localized high pH regions at the injection point, the alkali solutions had to be dilute, but this would be impractical from the standpoint of water consumption. Thus this approach appears to require a special mixer design to permit the use of concentrated additive solutions, or a technique for homogeneous precipitation in the brine.

Another approach to scale control that was examined briefly was the use of hydrogen peroxide to acidify the brine.¹⁰ It was thought that by oxidizing the ferrous ions in the brine to ferric ions, thus precipitating ferric hydroxide, a pH lowering could be achieved in a more economical manner than by the addition of hydrochloric acid. Hydrogen peroxide was chosen as the oxidant, because it was expected to react rapidly with ferrous ion, through the following series of reactions:

A "multiplication" factor thus could be created in which one mole of H_2O_2 would result in the consumption of four moles of hydroxide ion. On a strictly per-pound basis, this would be more economical than using HCl.

Concentrations of 25 and 50 ppm of H_2O_2 lowered the pH of the effluent brine to 5.3 and 4.4 respectively, along with the expected precipitation of ferric hydroxide. Our standard precipitation/incubation test at 90°C also showed that the reaction of H_2O_2 with the brine continued for at least 30 min., and silica was to some extent coprecipitated with the ferric hydroxide. Thus this technique does appear to be viable, but again at the cost of handling high suspended solids levels in the brine.

GENERAL COMMENTS ON TESTING SILICA
SCALE-CONTROL ADDITIVES IN GEOTHERMAL BRINE-HANDLING SYSTEMS

Prospective users of chemical additives for scale control in geothermal systems where silica is the major problem should be fully aware of the peculiarities of the fluid chemistry of these systems. In addition, some of the precautions common to the use of chemical additives in any industrial process should be taken into consideration.

The most important aspect of the evaluation and use of chemical inhibitors in the silica-scaling brines is the point of addition of the additive in the flow system. Lowering the pH of the brine by the injection of acid will immediately retard the polymerization of silica, and to the extent that the pH is lowered, this technique will effectively inhibit scaling at all points downstream. In contrast, the point of injection is much more critical in the case of the organic inhibitors, because the mechanism of inhibition is different. As noted above, based on our experience, it appears that, for effective inhibition of silica scaling, the additive must be present in the brine when the silica particles are of the order of $0.1\text{ }\mu\text{m}$ in size or smaller. It is thus very important to inject the chemical as early in the brine flow system as possible so the inhibitor can act on the silica particles in their incipient growth stage. (Not only will late injection be ineffective, there is even some evidence that the opposite effect of silica flocculation is induced when the additive is injected too late.) This means that the additive must be injected at a high temperature point in the geothermal energy conversion system.

In the case of systems employing a single stage (flash, brine/steam separation, or total flow concept), the additive must be injected upstream of the separator or nozzle. Even though the flow at that point is two-phase, concentrations of the additive in the effluent brine can still be maintained accurately enough on the basis of the known liquid fraction. Injection directly into the separator may be satisfactory in some cases if residence times in the separator are not too long and if the temperature is above $\sim 160^{\circ}\text{C}$.

If additives are evaluated at pre-existing facilities using a side-stream pilot system, the same recommendations apply. Ideally, the pilot system should have a single stage identical (in temperature, pressure, and residence time) to that of the main system, it should be operated from wellhead brine, and the additive should be injected at high temperature.

The caveats for additive injection in binary cycle systems would be essentially the same, especially in the case of the flashed binary type. For the direct binary cycle, where no flashing occurs, high-silica brines may still scale due to the temperature reduction; here the inhibitors should be injected well upstream of the problem areas.

High-temperature or wellhead injection of the additive is still the best approach even for dual-flash steam systems; however, on the basis of our pilot studies, which approximated this type of system, it appears that injection of the additive between the two flash stages is effective if the temperature of first flash is above $\sim 160^{\circ}\text{C}$. At that temperature, and for normal system residence times, the process of silica particle growth is probably not yet too far advanced for effective inhibition by the additive. However, it should be realized that the highest percentage of scale inhibition then occurs at the lower temperatures (where also the uninhibited rate of scale growth is largest). In situations where the temperature of scale formation is higher, the degree of silica supersaturation is lower, or other conditions favor the formation of a vitreous silica scale, additives which function by the mechanism of steric stabilization will diminish in effectiveness.

A knowledge of the brine and scale chemistry is of course essential in assessing the possible usefulness of a scale inhibitor program. The pH of the brine is a critical factor in the precipitation of silica and the action of the organic compounds. One of the first sets of data that should be developed in an additive testing program in which acid is to be used is a measurement of the buffer capacity of the brine, i.e., its change in pH vs quantity of added acid. This should be obtained by on-line injection "titration." If a calcite-type inhibitor (such as a phosphonate or acrylate) is to be used in the formulation, users should be aware of the danger of its precipitation with brine calcium if there is an overfeeding (concentrations above ~ 5 ppm).

Other seemingly minor details in the use of chemical additives can have an important bearing on the success of scale inhibition in a geothermal project. The chemical additive should be injected in a smooth, non-pulsating manner so that local, large variations in concentration do not occur at the point of injection. In the case of acid, this can cause severe corrosion; high concentrations of the organic compounds may cause a precipitation which is not reversible downstream. Likewise, consideration must also be given to the concentration of the additive in the feed solution. Here there is a tradeoff between the volume of additive solution (and water) consumed per day and the desire to ensure rapid mixing of the chemical in the brine.

CONCLUSION

The results of the studies outlined above represent several alternative approaches to mitigating the formation of scale from the Salton Sea Geothermal Field brines, but the use of chemicals for scale abatement is not yet an accepted technique in a practical situation. Interest in this area, however, seems to be growing, in spite of the rather large quantities of chemicals that might have to be used,²⁶ and the significant incremental cost of the chemicals. Several of the compounds mentioned herein have been confirmed as silica precipitation inhibitors in Japan and Mexico, and several water treatment and chemical companies are initiating searches for silica inhibitors that will probably lead to less expensive formulations. Treating the whole geothermal well flow is not out of the question, as evidenced by the work on scale inhibitors at other geothermal³⁴ and geopressured fluid resources where calcite, rather than silica, is the scaling compound. Although some of the worst effects of silica scaling may seem to have been avoided by other approaches, continued difficulties may lead workers to reconsider chemical treatments.

From an optimistic perspective, it appears that in the not-too-distant future, a reliable, profitable geothermal system could be constructed at the Salton Sea using a chemical brine treatment approach, provided the system encompasses the following features:

- A chemical brine treatment program involving the use of both an organic inhibitor (possibly a mixture) and moderate brine pH reduction by the use of hydrochloric acid. The organic compound(s) would be tailored to retard both silica precipitation (and CaCO_3 if necessary) and corrosion of the plant materials.
- Control of brine pH during acidification to within ± 0.3 pH unit.
- Judicious use of the low-cost, low-alloy steels that have been shown to be much more resistant to hypersaline brines than mild steel.⁸
- If the reactor/clarification process^{17,18} is used for reduction of the concentration level of dissolved silica prior to reinjection, the effect of the organic/acid scale inhibitor may have to be neutralized, but this could be easily accomplished.

Moderation of the formation of scale and suspended solids in the brine would result in a very "clean" process that would be much less aggressive toward process equipment, measurement devices, and controls.

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