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ON-LINE TESTS OF ORGANIC ADDITIVES FOR THE INHIBITION OF THE PRECIPITATION OF SILICA FROM HYPERSALINE GEOTHERMAL BRINE III. SCALING MEASUREMENTS AND TESTS OF OTHER METHODS OF BRINE MODIFICATION

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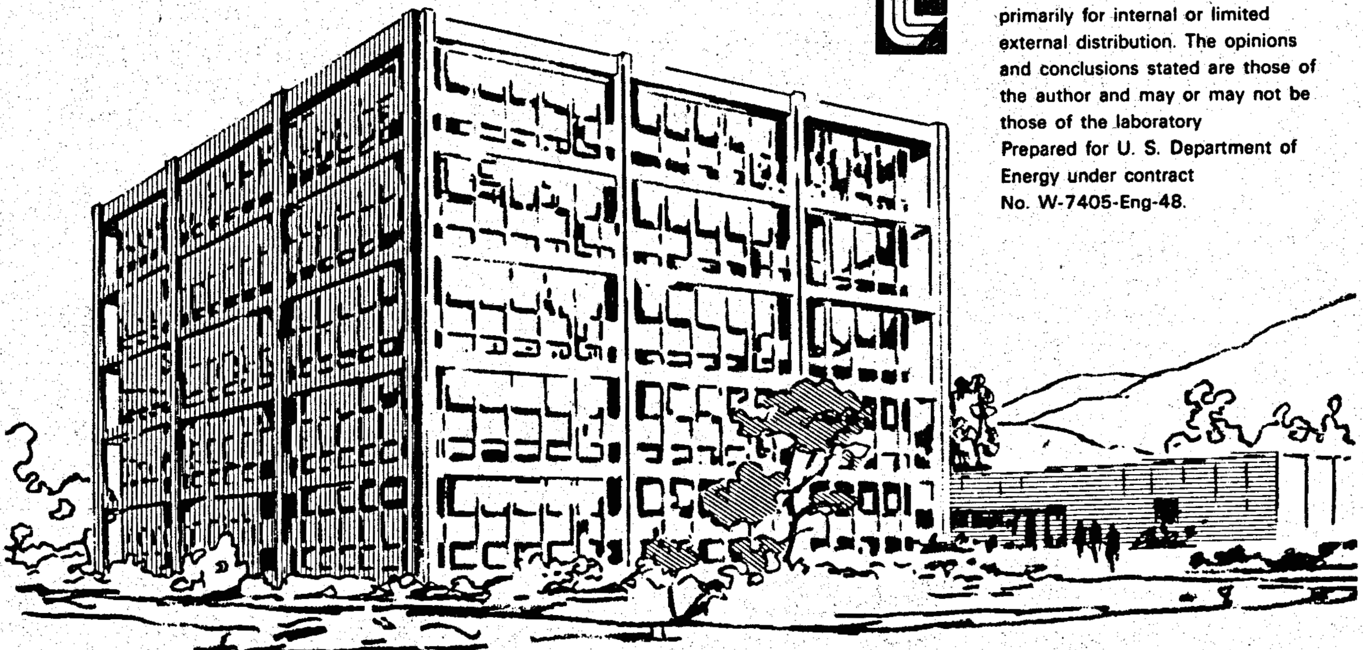

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Contents

Abstract

The Lawrence Livermore Laboratory Brine Treatment Test System at Niland, Imperial Valley, California, has been used to evaluate a promising organic compound as a scale control agent and to investigate several other approaches to the abatement of siliceous scale in brine handling equipment. Three-day scaling tests of Ethoquad 18/25 (Armak) alone (at a concentration of 25 ppm), and Ethoquad in combination with Dequest 2060 (Monsanto) showed a scaling rate reduction of 40-80% at 90°C, 15-40% at 125°C, and no reduction at 210°C. Changes in the salinity of the brine during the test series were found to have a pronounced effect on the rates of precipitation of silia and scaling, and on the effectiveness of the Ethoquad as an inhibitor. Additional data are reported on the reduction of scale by acidifcation with hydrochloric acid, and some of the effects of producing acidified brine by the addition of hydrogen peroxide were measured. The influence of brine salinity and pH (altered with sodium hydroxide) on the distribution of monomeric silica in the flash system was examined. Several new compounds were tested as silica precipitation inhibitors and one, PAE•HCl [Dynapol poly(aminoethylene, HCl salt)] , was found to be the most potent yet discovered. Proposals for future studies are outlined.

Introduction

This report presents further results of our field test program to evaluate organic chemical compounds as additives for the abatement of the scales formed from the brines of the Salton Sea Geothermal Field. Both scaling tests and off-line precipitation inhibitor measurements are described. Previous reports have dealt with off-line screening tests of generic chemicals,[1] the evaluation of the effect on scaling-rate of a series of proprietary chemical mixtures,[2] and on-line tests of a number of generic chemical compounds.[3-4]

Except for a longer-term evaluation of Natrosol 250LR,[2] most of the generic chemical experiments have thus far involved only relatively rapid screening tests in which the additives are injected into the flowing brine at high temperature (∿200°C), and then their effects on the silica in samples of the effluent brine (at ∿ 90°C) are measured. Positive results depend on two prerequisite characteristics of an effective antiscalant: resistance to the rigorous conditions of the brine and reactivity toward silica. However, these experiments do not permit direct estimates of the degree of scale reduction that can be achieved by active additives, especially at temperatures higher than those of the screening tests. For example, although polyoxyethylene polymers are effective inhibitors of silica precipitation at 90°C, it was found that their inverse solubility/temperature characteristic makes them ineffective at 125°C.[3]

On-line scaling tests (of as long a duration as possible) are thus required for a complete evaluation of candidate additives. It has become obvious from our testing that an extremely powerful precipitation inhibitor is required to bring about a significant degree of scale reduction. Scaling tests are considerably more severe because, as discussed previously,[4] the fluid shear in the turbulent, flowing brine and fluid impingement on the plant surfaces greatly enhance the aggregation of the scale-forming (silica) solids. The classical threshold-type inhibitors[5] have not been effective,[2] perhaps because there is very little crystalline material in the scales with which we are dealing -- all of the deposited silica is amorphous.

Our previous testing[1-4] revealed one class of compounds to be the most promising for scale reduction in hypersaline geothermal systems, that of cationic, nitrogen-containing compounds. This class includes the quarternary ammonium compounds, polyethylene imines, and tertiary amines. The presence of polyoxyethylene in these compounds also enhances their activity toward silica, but surfactant character per se does not appear to be a necessary characteristic. Among the cationic substances, strong ionic character is probably desirable because it contributes the solubility properties required by the high ionic strength of the brine, especially at high temperatures. Thus a quaternary ammonium compound, Ethoquad 18/25 (Armak Company), which is methylpolyoxyethylene(15) octadecylammonium chloride, emerged as the most powerful inhibitor of silica precipitation in our previous tests.

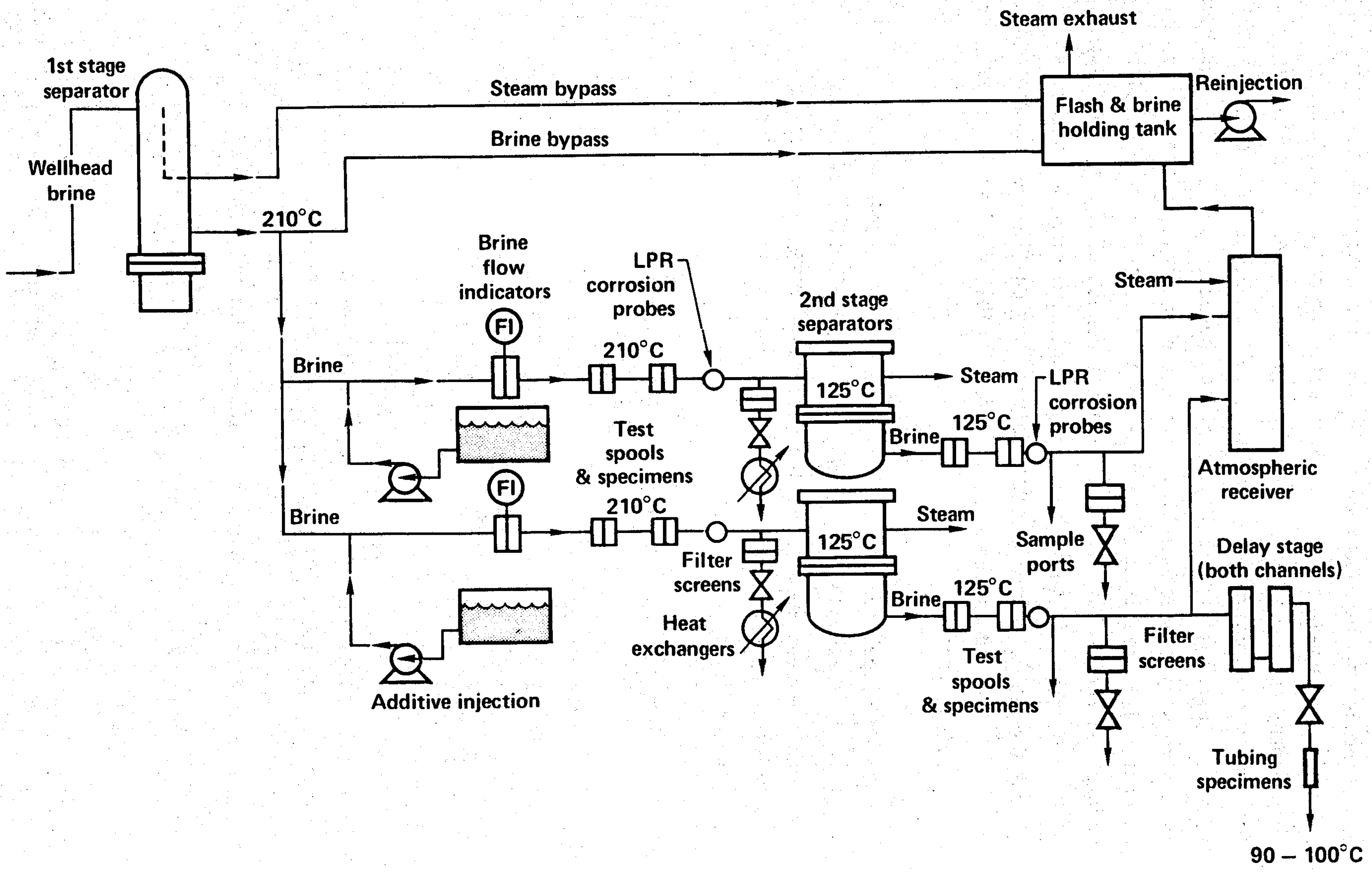
The principal subject of this report is a further evaluation of Ethoquad 18/25 as an antiscalant -- alone, and in combination with a phosphonate compound, Dequest 2060 (Monsanto Company). Some newer results and some previously unreported data on other approaches to brine modification also are discussed.

Experimental Technique

The additives were tested with Magmamax No.1 brine using the apparatus shown in Figure 1 and the techniques described previously.[2,3] Scaling rate measurements were made with the full complement of specimens, including sections of 1/2- and 1/4-in. tubing placed at the outlet of the delay stage to obtain data on scaling rates at 90°C. Measurements of the scaling rates on mild steel coupons were performed by placement of the coupons on 2-in. pipe plugs inserted near the Petrolite probes, instead of in the flanges of the 1-in. pipe spools as was done previously.[2] Precipitation tests were carried out on the effluent brine samples collected at the atmospheric flash temperature of 105°C and incubated anaerobically at 90°C.

FIGURE 1

SCALE-CONTROL TEST SYSTEM



Brine Characteristics

The scale abatement evaluations were planned to coincide with full-flow, one-well operation of the Geothermal Loop Experimental Facility (GLEF) of the San Diego Gas and Electric Company, so that high-salinity brine at constant conditions would be obtained. However, several events caused the composition of the brine to change considerably during the testing. This is illustrated in Figure 2. The salinity of the brine at the beginning of the test series (4.0 Mol/l chloride) was close to that observed during the test series of November and December, 1978, during which the GLEF was also in operation. On June 13, 1979 at about 1100, there began a swarm of earthquakes, with one of the first registering 4.2 on the Richter scale. Shortly thereafter, for a period of ∿1 h, the brine at the LLL facility was observed to contain a large amount of particulate matter, and the brine salinity was found to have increased.

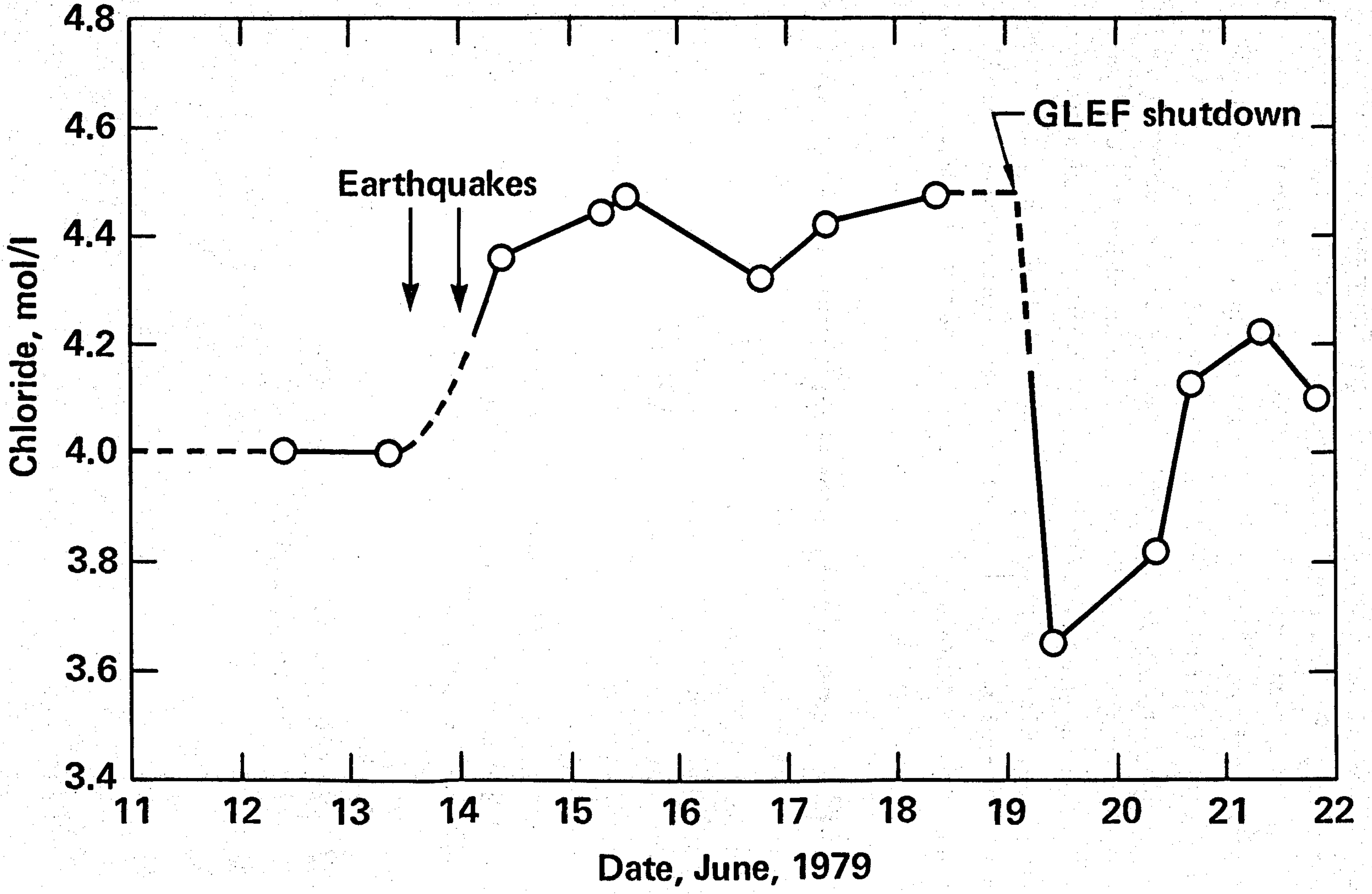
From that point on, while the GLEF remained in operation, the salinity of the brine was ∿4.5 Mol/l in chloride, which was the same level observed under corresponding well flow rates during 1977 and early 1978.[6] The Magmamax No. 1 wellbore was cleaned by reaming in May, 1978, following which the full-flow salinity of the brine decreased from ∿4.5 to ∿4.1 Mol/l chloride. As a result of, or coincident with the earthquakes, the brine has now apparently returned to its composition prior to the reworking of the well. These changes have an important effect on the rate of precipitation of silica,[6] the quantity of solids eventually precipitated from the brine,[6] and, as will be shown below, the scaling tendency of the brine.

At 4.0 Mol/l chloride, the total dissolved solids measured 20.7%; at 4.45 Mol/l chloride, 22.9%. The densities of these brines at 25°C were 1.164 and 1.180, respectively.

FIGURE 2

CONCENTRATION OF CHLORIDE IN BRINE DURING JUNE TEST SERIES

Magmamax No. 1 Brine Flashed to 105°C



As can be seen in Figure 2, when the GLEF ceased operation on June 19, 1979, the salinity of the brine -- flowing at the reduced rate at the wellhead -- dropped precipitously. The new level (3.5-3.8 Mol/l chloride) was typical[3,4,6] of that observed when we were the sole user of the well, but then the brine salinity rose again to a level that may be the new equilibrium value. Our experiments were terminated on June 22nd.

The wellhead pressure rose from ∿265 psia before the earthquakes to ∿ 280 psia from the 14th to the 19th, and then rose again to ∿330 psia after the GLEF shutdown. Wellhead temperatures during these intervals were 212, 216, and 222°C, respectively. An unusual feature of the brine characteristics was that the silica concentration remained virtually constant throughout the test series in the range of 483 to 509 mg/kg SiO_2.

Effect of Brine Salinity on Precipitation and Scaling Rates

The widely varying brine conditions encountered during the past year have afforded an opportunity to obtain quantitative data on the effect of brine salinity on the rate of solids and silica precipitation. In general, an increase in salinity decreases the equilibrium solubility of amorphous silica,[6] and this increases the rate at which it precipitates from supersaturated solution, either as suspended solids or as scale. This is in contrast to the behavior of lower-salinity brines in which the salt concentration does not affect the solubility of silica.[7]

Because of this sensitivity to the total dissolved salt content of the brines, the effects of chemical modification of the brine must be compared on an equal salinity basis. Table 1 lists data that show how the quantity of precipitated solids and the amount of silica that remains dissolved in the brine at 1 h varied with the salinity of the brine. As the salinity increases, the potency of inhibitors such as the Ethoquad 18/25 decreases dramatically, and the effect of salinity on the kinetics of silica precipitation can be distinguished even more readily with an inhibitor present than when the much less stable, untreated brine is examined.

Table 1. Effect of Brine Salinity on Rate of Precipitation of Silica and Solids in Untreated Brine and in Presence of Ethoquad 18/25 Inhibitor. (Magmamax No. 1 Brine; 1 h Incubation at 90°C)

Effluent Brine Chloride Concentration Mol/1	Concentration of Suspended Solids mg/kg	Silica Retained %
	Untreated Brine	
3.56	233	58
3.74	285	48
4.02	312	41
4.16	307	41
4.47	307	40
	20 ppm Ethoquad 18/25	
3.63	55	96
3.84	53	92
4.02	79	85
4.16	175	69
	20 ppm Ethoquad 18/25 + 5 ppm Dequest 2060	
4.32	271	60
4.47	283	53

Not surprisingly, increasing the salinity of the brine also has an equally dramatic effect on the scaling tendency of the brine, especially in the lower temperature range. This is illustrated in Table 2, which summarizes the scaling rates observed for essentially three levels of salinity: 3.6, 4.0, and 4.5 Mol/l chloride. The tests during November and December, 1978, were both run at the intermediate condition. An increase in brine salinity from 3.6 to 4.5 Mol/l chloride increases the scaling rates at the lower temperatures by at least a factor of five. This increase cannot be due entirely to changes in brine silica concentration, which, for the respective salinities, varied from ~450 to ~500 mg/kg. Also, if past results[6] hold true for the high-salinity brine encountered here, the highest scaling rate cannot result from a change in the concentration of another minor constituent of the brine. Rather, it must be due to the increased "salting out" effect of the increased sodium, potassium, and calcium chlorides in the brine.

The differences in the values of scaling rates for the three materials are partly due to the fact that the accumulation of solids on the mild steel results from both corrosion and "pure" scaling, and from differences in the adhesion of scale on the three surfaces. However, at higher scaling rates and at longer exposure times, these differences should equalize as the newly forming scale "sees" only a scaled surface. With these relatively short exposure times, the scaling rates measured on the inert Teflon and Hastelloy surfaces are probably the most indicative of the long-term scaling behavior of the brine.

Scaling Rate Tests of Ethoquad 18/25

Prior to commencement of the 3-day tests of Ethoquad 18/25 as a scale inhibitor, additional off-line precipitation tests were carried out at the then existing brine conditions to determine the effect of changes in the concentration of Ethoquad on its action as a colloid stabilizer. These data are summarized in Table 3 and Figure 3. As can be seen for 4.0 Mol/l chloride brine, there is a steady decrease in activity of the Ethoquad as its concentration is lowered; however, the most significant decrease occurs below 20 ppm. Thus a concentration of 25 ppm was selected for the first scaling test.

Table 2. Effect of Brine Salinity on Scaling Rates in LLL Brine Treatment System (Untreated Magmamax No. 1 Brine)

				Scaling Rate, mil/h						
				Coupon, 210°C			Coupon, 125°C			Tubing, 9
Date	Channel	Effluent Brine Chloride Concentration Mol/l	Time of Exposure h	Mild Steel	Hastelloy	Teflon	Mild Steel	Hastelloy	Teflon	Mild Stee
Mar 79	A	3.5-3.7	88	0.05	0.02	0.02	0.10	0.03	0.04	1.2[b]
Dec 78	A	4.0	65	0.08	0.02	0.03	0.38	0.06	0.09	-
Nov 78	B	4.0-4.1	113	0.02	0.01	0.05	0.21	0.10	0.11	-
Jun 79	A	4.0-4.5[a]	69	0.10	0.03	0.06	0.78	-	0.68	4.8[c]

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[a] Most of time at higher value; see Figure 2.

[b] Exposure for 21 h.

[c] Exposure for 13 h; 4.0 Mol/l chloride.

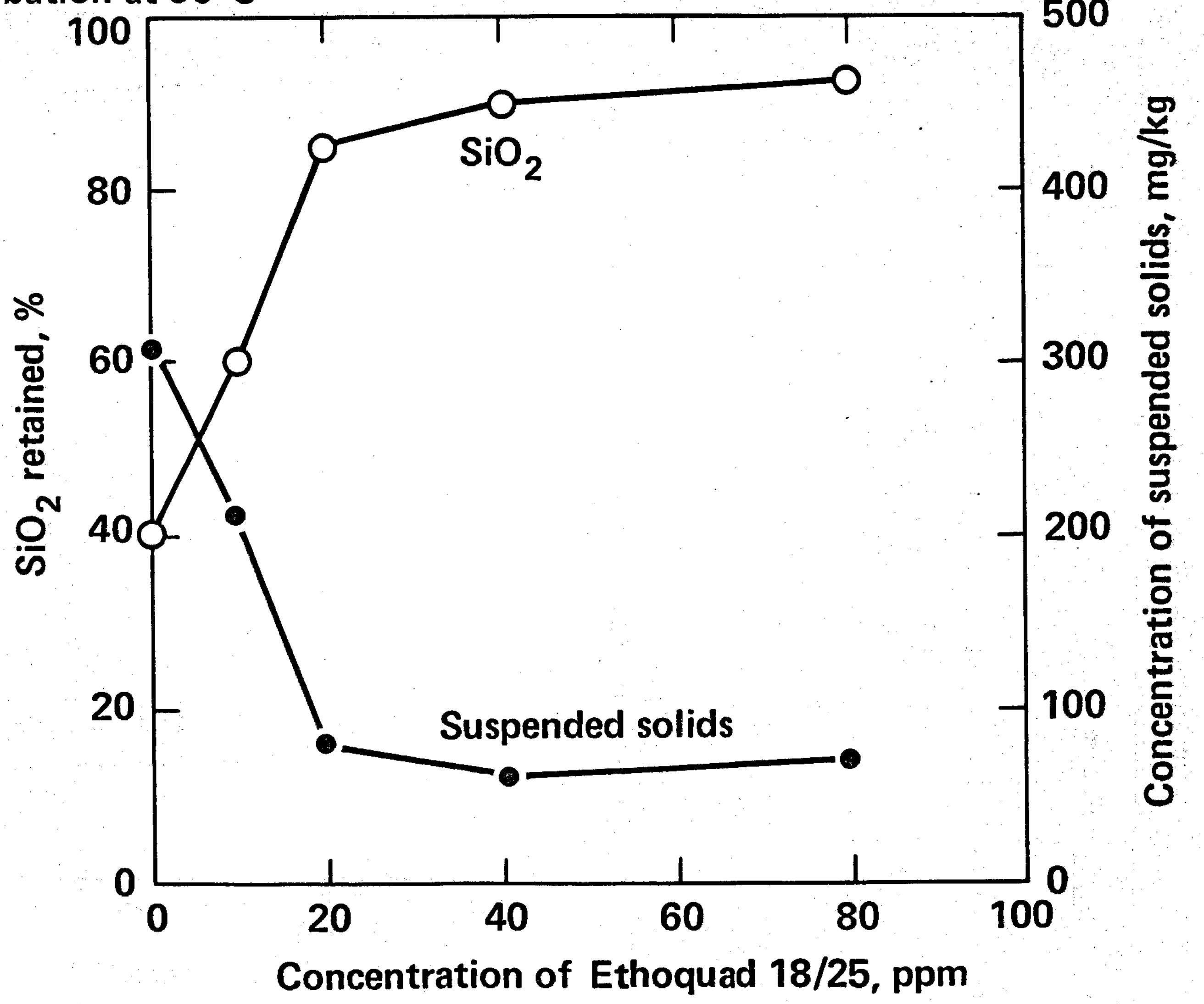
Table 3. Effect of Concentration of Ethoquad 18/25 on the Precipitation of Solids and Silica from Geothermal Brine at 90°C. (Magmamax No. 1 Brine, 4.0 Mol/l Chloride.

Incubation Time	Concentration of Suspended Solids, mg/kg					Concentration of SiO_2 in Filtrate, mg/kg				
	0 ppm	10 ppm	20 ppm	40 ppm	80 ppm	0 ppm	10 ppm	20 ppm	40 ppm	80 ppm
0	0	0	0	0	0	505	505	496	483	505
30 min.	295	63	51	39	49	239	478	450	472	496
1 h	312	212	79	61	70	208	303	422	437	465
2 h	332				129	202				395

FIGURE 3

EFFECT OF CONCENTRATION OF ETHOQUAD ON PRECIPITATION OF SILICA AND SOLIDS

1 h Incubation at 90°C



In addition to a scaling test of Ethoquad 18/25 alone, a combination of 20 ppm Ethoquad 18/25 and 5 ppm Dequest 2060 (Monsanto diethylenetriamine pentamethylene phosphonic acid) was also tested in a 3-day run. Although Dequest 2060 has exhibited only weak activity toward silica in precipitation tests,[3] and it is primarily used only for crystalline deposits such as $CaCO_3$, $BaSO_4$, and $CaSO_4$,[5,8] we thought it might have a synergistic effect on the hypersaline scales in combination with a silica inhibitor such as Ethoquad.

Three 3-day scaling tests were conducted during the June test series and the results are given in Table 4. The control test with untreated brine and the test with 25 ppm Ethoquad were conducted simultaneously in channels A and B of the test system, and the "strong" brine condition (coincident with the earthquakes; see Figure 2) prevailed during the last ~48 h of the run. The Ethoquad/Dequest-combination test was carried out June 16-19, entirely during "strong" brine conditions.

Assessment of the results of the scaling tests is complicated by (a) some indications on several previous occasions that the two channels of our system are not perfectly identical, and (b) the fact that comparison of results obtained with the same channel means different times and different brine conditions. Nevertheless, some important effects are clearly evident in the data of Table 4. At 210°C, in the test with Ethoquad alone, the increased scaling rates were due mostly to the accumulation of a gray-colored powdery material that was largely silica. It did not appear again in the subsequent test in channel A with the Ethoquad/Dequest mixture, thus it may have resulted from the particulate influx that occurred after the earthquakes. However, even the Ethoquad/Dequest combination appeared to increase the high temperature scaling rates somewhat, and this is a possible effect that must be carefully evaluated before an additive can be recommended without qualification. Several of the proprietary additives previously tested[2] definitely had the detrimental effect of causing a high temperature deposit. A lower temperature point of injection would be mandatory in such cases if the additive successfully diminished the low-temperature silica scales. Thus far, we have not found any organic additive that clearly <u>reduces</u> the predominantly sulfide scale formed at 200°C.

Table 4. Effect of Additives on Scaling Rates of Geothermal Brine (Magmamax No. 1 Brine, 4.0 - 4.5 Mol/l Chloride; June, 1979 Test Series)

			Scaling Rate, mil/h						
			Coupon, 210 C			Coupon, 125 C			Tubing, 90 C
Additive	Channel	Time of Exposure h	Mild Steel	Hastelloy	Teflon	Mild Steel	Hastelloy	Teflon	Mild Steel
None, Control	A	69	0.10	0.03	0.06	0.78	-	0.68	4.8[a]
Ethoquad 18/25 (25 ppm)	B	69	0.41	0.20	0.14	0.67	0.42	0.51	2.7[a]
Ethoquad 18/25 (20 ppm) + Dequest 2060 (5 ppm)	A	66	0.15	0.08	0.10	0.44	0.53	0.53	0.9[b]

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[a] 4.0 Mol/l chloride; 13 h exposure.

[b] 4.5 Mol/l chloride; 24 h exposure.

At 125°C, the results indicate that the additives tested do retard the formation of scale, but not to a very great extent. It appears that the Ethoquad 18/25 is the active compound, and that the Dequest 2060 conveys no additional beneficial effect. The reduction of the rate of scaling on the mild steel coupons ranged from 15-44% for the two additive runs in comparison with the untreated brine. For the Teflon coupons the reduction was 22-25%. The values for Hastelloy appear similar to those for Teflon, but the coupon exposed in the control test was dislodged and lost for purposes of comparison. The scale formed at 125°C in the presence of the Ethoquad was different in color and consistency compared to that formed from untreated brine. The Ethoquad-treated brine formed scale that was nearly colorless (vs. the normal yellow-brown) and it was easier to scrape off the specimen surfaces. Chemical analyses and microscopic examinations yet to be performed may reveal the nature of these observations.

The scaling rates shown for 90°C in Table 4 were obtained by flowing the brine through 1/4-in. steel tubing at a flow rate of 0.5 l/min. This tubing was connected to the exit of the delay stage, (see Figure 1) which has the effect of aging the brine and dropping its temperature from 125°C. Very little, if any, brine flashing occurs in the specimen. The scale formed here is typical of that found in atmospheric receivers and downstream equipment -- generally very porous and granular in appearance, and very fragile when dry.

The data of Table 4 show that the additives significantly reduce the rate of growth of the 90° scale, but the precise factor of improvement is somewhat uncertain. With the Ethoquad alone, tested at the same time as the control in the other channel, there was a 44% reduction in scaling rate. With the Ethoquad/Dequest combination, there was an 81% reduction compared to the control. This is quite encouraging because this test was carried out under the strongest brine conditions and is based on a comparison of results for the same system channel. The data also suggest that, in contrast to 125°C, there may be an advantage in using Dequest 2060 with the Ethoquad. The 90°C scales are being further examined for their detailed morphology and chemical composition.

Viewed over the whole temperature range, the degree of scale inhibition afforded by our best additives is still not very attractive economically, although the greatest abatement does occur where the scaling tendency of the untreated brine is highest. The results at least bear out again the validity of the precipitation screening tests, and these experiments represent another step toward finding the most powerful scale inhibitor that is possible in an organic compound.

Scaling Rates of Acidified Brine

Acidification with hydrochloric acid has been established[9] to be effective in reducing the hypersaline brine scales. This method was evaluated subsequently in a long-term test using a four-stage flash system.[6] The average pH of the brine during this test was 4.5 and the salinity of the brine was for the most part in the range of 4.0-4.5 Mol/l chloride. The observed degrees of scaling-rate reduction were: at 210°C, 95%; 150°, 87%; 125°, 60%; and 105°, 88%.[6]

The presently configured brine-treatment test system (see Figure 1) has also been used for additional tests of acidification to compare the results with those obtained with the organic additives. Some of these results, which were obtained during "weak" brine conditions, are listed in Table 5 together with measurements for the untreated brine. 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. The 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 Table 5 it can be seen that more scale formed on the mild steel coupons at pH 5 than in the untreated brine, and much of this scale was (in contrast to that of pH 3) silica or silica/sulfide rather than corrosion product. This is attributed to the fact that corrosion of the steel neutralizes the acid in the vicinity of the metal and renders the brine more heavily scaling again. Acidification to pH 3 overcomes this effect -- corrosion product constantly dissolves away into the flowing brine, bare

Table 5. 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, 210°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

metal is constantly exposed, very little solid reaction product accumulates on the surface, and silica precipitation is greatly suppressed. Quite high corrosion rates were also observed at pH 3 (see below). Incomplete experiments at pH 4 indicated that this pH also is not low enough to completely overcome the surface neutralization of the acid.

Be that as it may, these observations are probably just peculiar to the short exposure times employed. After several hundred hours exposure, and the accumulation of more scale, the chemical reactions occurring near the surface should become less influential on the newly forming scale. And, as discussed before, the scaling rates of the mild steel should approach those observed for the inert materials. Scaling rates based on over 500-h exposures[6] do not show such dramatic differences among materials. Work could be done in defining these effects more carefully; meanwhile, the uncertainties of predicting or extrapolating scaling rates where both corrosion and precipitation processes occur together should be clearly understood.

Electrochemical Corrosion-Rate Measurements

Estimates of the corrosion rates of AISI 1018 mild steel were obtained during the scaling rate tests by means of Petrolite Instruments Company linear-polarization-resistance (LPR) equipment. LPR probes were located (see Figure 1) in both the 210° and 125°C portions of the system. The results of these measurements for the Ethoquad additive, brine acidification, and several control experiments (untreated brine) are listed in Table 6. The results are consistent with the scaling-rate observations. Brine acidification caused high corrosion rates at 210°C; portions of the pH 3 specimens were etched away during the test so that the indicated 40-mpy corrosion rate seems conservative. Accumulation of silica scale at 125°C on the pH 5 specimen (as discussed above) probably caused the measured corrosion rate to be not significantly different from that of the untreated brine. Corrosion rates in the presence of Ethoquad are also not significantly different, which correlates with the amount of scale that formed during these experiments. If all four of the control experiments can be considered equivalent, they provide a good indication of the reproducibility of this measurement.

Table 6. Steady State Corrosion Rates of Mild Steel (AISI 1018) Estimated by Linear Polarization Resistance Technique

Brine Conditions	Corrosion Rate, mpy[a] 210°C	125°C
Control, Nov 78	7	15
Control, Dec 78	9	14
Control, Mar 79	11	7
Control, June 79	4	22
Acid, pH 5	75	8
Acid, pH 3	40	120
Ethoquad 18/25	10	6
Ethoquad/Dequest	6	2

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[a] Value reached after >60 h exposure.

Effect of Hydrogen Peroxide on the Brine

Another method that has been proposed for lowering the pH of the brine, and thereby possibly reducing the rate of scaling, is an indirect method involving the addition of an oxidizing agent. By oxidizing the ferrous ions in the brine to ferric ions thus precipitating ferric hydroxide, it has been thought that a pH lowering could be achieved in a more economical manner than by the addition of hydrochloric acid.

We tested this concept briefly using hydrogen peroxide as the oxidant, chosen because it was expected to react rapidly with ferrous ion, through the following series of reactions:

$$\begin{array}{l} H_2O_2 + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2OH^- \\ 2Fe^{3+} + 6OH^- \rightarrow 2Fe(OH)_3\downarrow \\ \hline H_2O_2 + 2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_3\downarrow \end{array}$$

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.

Hydrogen peroxide was metered into the brine as a dilute solution in the same manner as the additives to obtain concentrations of 25 and 50 ppm. The effluent brine was also collected in the usual manner, incubated, and analyzed for suspended solids and concentration of dissolved silica. At both dosages, the hydrogen peroxide produced a distinct rust-colored turbidity, and the results of the analyses are listed in Table 7. It can be seen that a relatively small amount of hydrogen peroxide does result in a substantial pH reduction. Under comparable conditions ~200 ppm HCl would be required to reach pH 5. At the time of sampling, in the presence of 25 ppm H_2O_2, only 78% of the original silica remains dissolved, and at both dosages, the dissolved silica (and pH) continue to decrease with time. Thus final equilibrium does not appear to exist under these conditions, and although the analyses of the suspended solids have not been completed, it also appears that silica is coprecipitated by the $Fe(OH)_3$. Otherwise, at these low pH values, the dissolved silica would not be expected to disappear so rapidly.

Table 7. Effect of Hydrogen Peroxide on Brine Characteristics (Magmamax No. 1 Brine; 4.4 Mol/l Chloride, 503 mg/kg Total Initial SiO_2; Untreated Brine pH = 5.7; Incubation at 90°C).

	50 ppm H_2O_2			25 ppm H_2O_2		
Incubation Time, h	Brine pH	Concentration of Suspended Solids, mg/kg	Silica Retained %	Brine pH	Concentration of Suspended Solids, mg/kg	Silica Retained %
0	4.44	-	-	5.30	129	78
0.5	4.14	234	86	5.06	258	60
1	3.93	263	78	4.95	329	46

Both the scavenging of the silica by the $Fe(OH)_3$ and the lowered brine pH would be expected to decrease the conventional scaling rate. However, like the sludge seeding approach,[2] and other techniques that involve deliberate increases in the amounts of suspended solids in the brine, full-scale scaling tests are needed to assess the true worth of hydrogen peroxide as an additive for scale control. Moreover, equipment difficulties due to plugging always occur much more frequently in our system when solids are present in the brine, thus reliable experiments of this type will require more careful selection of components.

Effect of Sodium Hydroxide on the Brine

As was speculated in a previous report,[4] one of the reasons why significant reduction of the 125°C scale has not been achieved by the use of organic additives may be that the bulk of the scale is formed directly from monomeric silica. The organic additives probably act by adsorbing on rather large (0.01-1 μm) polymeric silica particles, and these represent only a small fraction of the total silica at the higher temperatures. Data were obtained previously[4] on the distribution of monomeric silica in our system and it was found that 90% of the silica was monomeric at 125°C.

In the present test series we investigated two methods for decreasing the fractions of monomeric silica in the system. One was raising the pH of the brine by the addition of sodium hydroxide. This would be effective if increasing the pH of the brine from its present value increases the rate of polymerization of silica. A similar approach using ammonium hydroxide has been proposed for scale control.[10] However, raising the pH is another of the techniques that undesirably increase the suspended solids concentration of the brine.

A second approach that we tested was to decrease the brine flow rate in one channel of the system by a factor of two, with all other conditions held constant. This increases the residence time of the brine, and the additional delay was expected to allow significantly more time for the silica to polymerize.

The results of the caustic addition and decreased flow rate experiments are summarized in Table 8 together with several measurements of untreated brine. One of the largest effects observed was that resulting from the earthquake-stimulated increase in brine strength to 4.4 Mol/l chloride. This decreased the monomeric silica to 80 and 59%, respectively, at 125 and 90°C. Subsequent tests were conducted with 4.1-Mol/l chloride brine. With this brine, as can be seen in Table 8, decreasing the flow rate had essentially no effect on the monomeric silica. This result is not totally surprising because many investigators (see, for example, Reference 11) report that the polymerization of silica involves an induction period, and we may not have exceeded it by the additional delay (in the second stage flash vessel: 4.6 vs. the normal 2.3 minutes). This experiment is worth repeating with a greater range of residence times because this is a widely varied parameter in geothermal systems.

Raising the pH of the brine with sodium hydroxide, like lowering the pH with acid, requires a significant amount of chemical because of the high buffer capacity of the brine. The turbidity of the brine that was observed during these experiments also suggests that metal hydroxides [such as $Fe(OH)_2$] were precipitated with just a slight pH increase. However, only a small increase in pH is required to affect the concentrations of monomeric silica. The pH rise of 0.3 unit produced by 100 ppm NaOH would probably produce a significant change in the nature of the scaling at 125°C, and, aside from the effect of pH on the polymerization of silca, the scaling would also be influenced by the presence of the additional suspended solids in the brine. This technique of brine modification should be investigated further with regard to scaling, and other alkalis such as ammonium hydroxide[10] and lime (CaO) should be tested. Also of interest would be the effect of a combination of alkali (to produce polymeric silica) and an organic inhibitor (to inhibit flocculation) on the scaling rates.

Tests of Other Organic Compounds as Precipitation Inhibitors

At the conclusion of the June test series, several new compounds were examined as precipitation inhibitors and these results are given in Table 9. The results for Ethoquad 18/25 in the same brine are listed for comparison, but they cannot be compared directly to previous precipitation-inhibitor results[3,4] because of the stronger brine.

Table 8. Effect of Salinity, pH, and Flowrate of Brine on the Distribution of Monomeric Silica in the LLL Brine Treatment Test System

		210°C Output of 1st Stage Separator	125°C Output of 2nd Stage Separator		90°C Output of Delay Stage		
Date	Effluent Brine Chloride Concentration Mol/l	Monomeric SiO_2, %	Brine pH	Monomeric SiO_2, %	Brine pH	Monomeric SiO_2, %	Remarks
May 79[a]	3.7	85	5.90	90	5.90	71	Control, no additive
17 Jun 79[b]	4.4	91	5.82	80	5.82	59	Control, no additive
21 June 79[c]	4.1	-	5.89	93	5.84	62	Control, no additive
21 June 79[c]	4.1	-	5.85	86	-	61	One-half flow rate
21 June 79[c]	4.1	-	5.98	74	5.87	61	50 ppm NaOH
21 June 79[c]	4.1	-	6.16	62	5.77	49	100 ppm NaOH

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[a] Total SiO_2, mg/kg: 1st Stage - 455; 2nd Stage - 468.

[b] Total SiO_2, mg/kg: 1st Stage - 424; 2nd Stage - 504

[c] Total SiO_2, mg/kg: 2nd Stage - 491

Table 9. Results of Precipitation Inhibitor Tests.
(Magmamax No. 1 Brine, 4.2 Mol/l Chloride; 20 ppm Additive)

Additive Trade Name	Manufacturer	Chemical Name	Brine Characteristics after 1 h incubation at 90°C: Concentration of Suspended Solids, mg/kg	Brine Characteristics after 1 h incubation at 90°C: Silica Retained, %
Control, No additive			307	41
Ethoquad 18/25	Armak	Methylpolyoxyethylene(15)-Octadecylammonium Chloride	175	69
PAE•HCl	Dynapol	Poly(aminoethylene, HCl salt)	100	89
XZ-8-5061	Dow-Corning	Quaternary-ammonium-functional silane	249	44
Belclene 200	Ciba-Geigy	Low M.W. polycarboxylic acid	283	48
Pyronate 40	Witco Chemical	Low M.W. alkyl aryl sulfonate	305	41
Glyoxal	J. T. Baker	Ethanedial	311	39
	J. T. Baker	Ammonium Molybdate[a]	330	39

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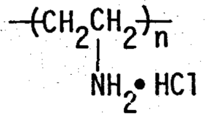
[a] Added 100 ppm as Mo(VI)

The new compound PAE•HCl (Dynapol), which has the structure



$$-\!\left(CH_2\underset{\underset{\displaystyle NH_2\cdot HCl}{|}}{C}H_2\right)_{n}\!-$$

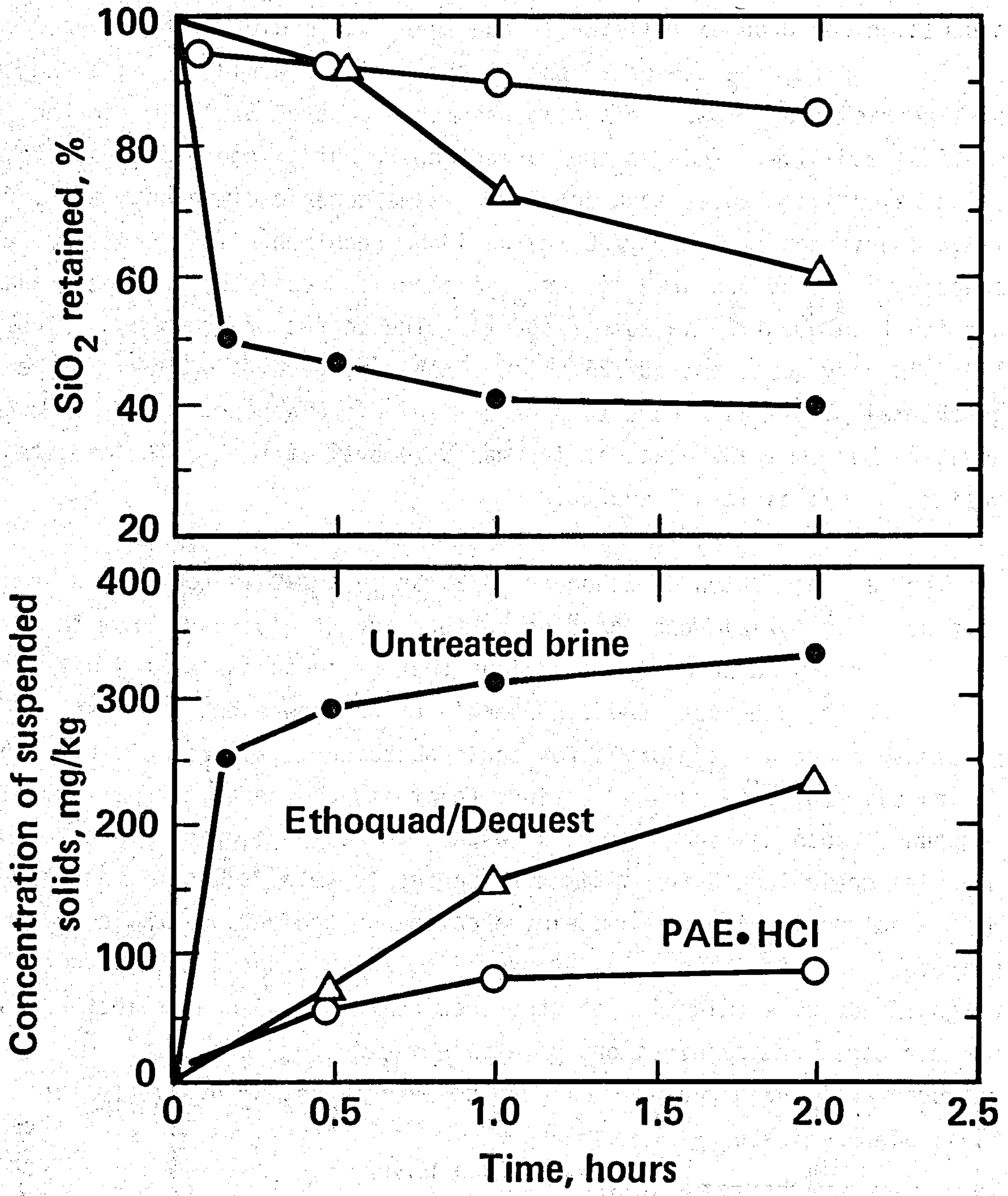
and a peak-average molecular weight of 120,000, stands out in these tests as a much more powerful inhibitor than Ethoquad 18/25, especially in this stronger brine. Figure 4 shows precipitation kinetics curves for PAE•HCl in comparison with untreated brine and the Ethoquad/Dequest combination used for the scaling test run. The potency of the PAE•HCl is somewhat surprising because its molecular weight is above the range that appears to be optimum for the polyoxyethylenes, polyethylene imines, and polyethyloxazalines.[4] On the other hand, it is a strongly cationic substance of the general type previously found to be active.[4] Other molecular weights of the PAE•HCl should be tested in future work. Also to be investigated further is the observation that this compound caused a slight turbidity in the effluent brine. The existing level of suspended solids could not be measured because of filter plugging, but the dissolved silica concentration was found to have dropped slightly ($\sim$5%) in a prompt sample at 125°C. It appears that PAE•HCL initially induces some precipitation of the silica (and/or metal compound), but then further precipitation is strongly inhibited.

None of the other compounds tested (see Table 9) had a significant effect on the precipitation of silica. The quaternary-ammonium-functional silane is another in the series of experimental silanes tested previously.[4] The Belclene 200 and Pyronate 40 are proprietary additives used in other water treatment applications, and like all previously tested anionic compounds, showed no activity. Glyoxal is a compound that showed some promise in our first off-line bench tests,[1] but it failed here. Lastly, ammonium molybdate was tried because of its known ability to form strong silicomolybdate complexes. Its failure is not too surprising, however, because the reaction of molybdenum and silicon species is most rapid at pH 2 and a stoichiometric reaction is required in which the Si:Mo ratio is 1:12 (Reference 12).

FIGURE 4

INHIBITION OF PRECIPITATION OF SOLIDS AND SILICA FROM GEOTHERMAL BRINE BY ORGANIC ADDITIVES

20 ppm Additive; Incubation at 90°C



Conclusions and Proposals for Future Work

The performance of Ethoquad 18/25 as an antiscalant in our tests can be characterized as quite promising and probably justifies further tests in a larger scale facility. The cost of its use appears favorable in comparison with the cost of electricity that could be generated from the brine. Assuming for the Salton Sea Geothermal Field that the cost of power generation would be 33 mill/kWh,[13] and that 1 kW could be generated from 100 lb of brine, the use of 20 ppm of the additive would increase the cost of electricity by ~6%. This also assumes a cost of $1.00/lb for the chemical additive. This is the current cost, but it could be less expensive since several companies manufacture the same generic compound,* and very large quanitites (1 ton/day/50 MW) would be required. This cost of the treatment must be measured against the benefits received, and these are difficult to quantify in some respects. The degree of scale reduction below 100°C is very good, but at 125°C it is not very good. However, since geothermal plants will have to undergo periodic cleaning, use of an organic additive has some advantage if its makes removal of the scale deposits easier as well as less frequent.

The recommendation of Ethoquad 18/25 as an additive for silica scale control is an interim one, pending further investigations. From the material presented here, it is obvious that Ethoquad has some limitations, and it, and related compounds, certainly do not represent the best foreseeable organic additives for scale abatement. Avenues of research that definitely should be pursued include (a) tests of the quaternary ammonium compounds (such as Ethoquad) with respect to ethylene oxide content and nonpolar chain length for optimum response; (b) evaluation of the response of the polymeric nitrogen-containing compounds (polyamino-ethylene, polyethylene imine, and polyethyloxazaline) with respect to molecular weight; and (c) examination of other new compounds such as thioethers and polymers that are combinations of ethylene oxide and cationic, nitrogen-containing chains. All of these tests would involve commercially - available chemicals.

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*e.g., Tomah Products Q-18-15

In addition, it would be fruitful to examine, as we have already suggested, a combination of the best organic inhibitor(s) with adjustment of the pH of the brine. For example, with mild acidification, a silica inhibitor should act to suppress the growth of scale during corrosion of the carbon steels that occurs as a result of surface neutralization of the acid. Many of the compounds we have found to be silica precipitation inhibitors are known to be corrosion inhibitors and this possible benefit also needs to be assessed. A fundamental study of the exact nature of the interaction of the proven precipitation inhibitors would also surely lead to the specification or selection of a better additive.

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