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PRELIMINARY RESULTS OF TESTS OF PROPRIETARY CHEMICAL ADDITIVES, SEEDING, AND OTHER APPROACHES FOR THE REDUCTION OF SCALE IN HYPERSALINE GEOTHERMAL SYSTEMS

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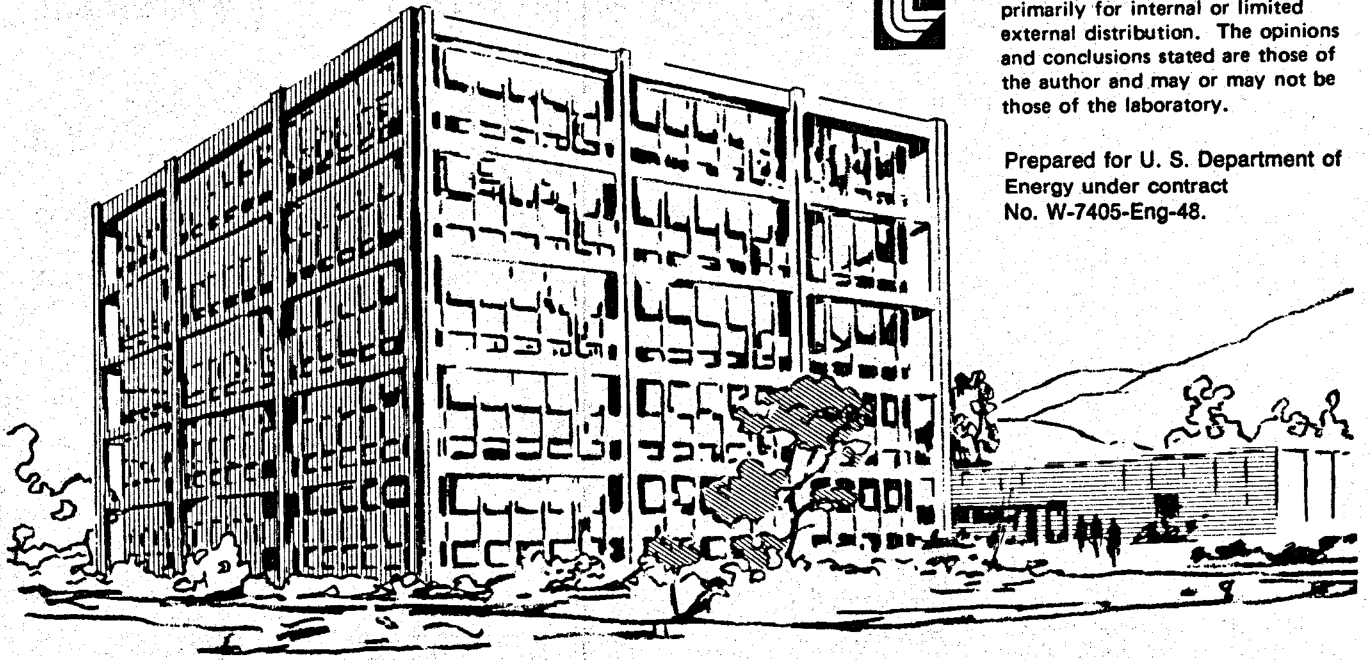

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Preliminary Results of Tests of Proprietary Chemical Additives, Seeding, and Other Approaches for the Reduction of Scale in Hypersaline Geothermal Systems

J. E. Harrar, F. E. Locke, C. H. Otto, Jr., S. B. Deutscher,
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Abstract

The LLL field brine-scaling test system and a variety of measurement techniques have been used to test a group of eight proprietary additives from eight different companies, a hydroxyethylcellulose previously found to retard silica precipitation, and geothermal sludge as a seeding agent to reduce scaling. For each additive, scaling rates at both 210 and 125°C and on three different materials -- mild steel, Teflon, and Hastelloy C-276 -- were measured using test coupons. Sections of steel pipe and perforated screens also were exposed to the treated brine, silica precipitation rates in the effluent brine were measured by means of the electrochemical linear polarization resistance technique. Examination of the pipe sections and chemical analyses of the scales are not complete, thus only preliminary conclusions are reported here. It appears that, although none of the additives effected a dramatic reduction in scaling rates, several decreased the rate of scaling of mild steel at 125°C by a factor of 2 to 3. Only hydroxyethylcellulose retards the rate of precipitation of silica in the effluent brine. Scaling rates could not be measured accurately in the seeding experiment because of its short duration, but this brine treatment had the desired effect, at 125°C, of reducing the level of dissolved silica and hence the scaling tendency of the brine. Further experiments of this type will be conducted.

Introduction

The accumulation of scale in industrial power generation, chemical, and petroleum processing equipment has been a problem for many years, and numerous chemicals have been developed for the abatement of such deposits.[1] Some progress has also been made in the control, by chemical means, of scales such as those formed from low-salinity geothermal brines. For example, brines such as those found at East Mesa, Imperial Valley, California, form deposits rich in calcium carbonate, and these have been found to be considerably retarded by the addition of small amounts of the compound diethylenetriaminepenta-methylenephosphonic acid (Monsanto Chemical Company "Dequest 2060") to the brine.[2] Studies of some other geothermal fluids and other industrial systems have shown that, in general, the phosphonate-type compounds are effective in controlling scales formed from crystalline compounds such as $CaCO_3$, $CaSO_4$, and $BaSO_4$.

In contrast, the brines of the Salton Sea Geothermal Field, in the vicinity of Niland, California, produce scales that, at high temperatures, are rich in metal sulfides, and at low temperatures, are rich in amorphous silica. Except for brine acidification,[3] no chemical treatment has yet been demonstrated to effectively inhibit these scales. The work reported here is a continuation of an effort to find a chemical additive, or mixture of compounds, that will economically retard the formation of Niland-brine scales. Primary attention is being directed toward the inhibition of silica-rich scales, because even at the high temperatures, silica is believed to influence the adherence of the sulfide scales. Moreover, the rate of the growth of the low temperature, silica-rich scales is much greater than that of the sulfide scales.

The chemical additives being tested are divided roughly into three groups:

- Proprietary chemicals and mixtures (the exact identity of which are trade secrets) that have been used, or are recommended for use as scale or deposit inhibitors in water systems.
- Specific chemical compounds (also commercially available in bulk quantities) selected on the basis of some knowledge of the organic functional groups found to be active toward silica in geothermal brine.[4]
- Cellulose derivatives, one of which, hydroxyethylcellulose (in the form of "Natrosol 250LR," Hercules, Inc.) has been demonstrated several times[4-5] to retard the rate of silica precipitation from geothermal brine.

A total of forty-nine specific chemical compounds were screened in a series of bench tests reported previously.[4] In July of 1978, several of the most promising of these substances, some functionally-related chemicals, and Dequest 2060 were examined under plant-type conditions in a field, brine-scaling test apparatus operating from Magmamax No. 1 well.[5] These tests were not completely definitive because of their short duration (~22 h for each additive) and because of the lowered brine salinity due to the low flow rate of the well. However, some of the test methods were validated, and they did reveal again a significant stabilization of colloidal silica at 90°C by hydroxyethylcellulose.

In the phase of the work reported here, the primary task was to test a group of proprietary scale control products that were recommended to us by various chemical companies on the basis of information that we supplied to them regarding the characteristics of the Niland brine and the deposits that are formed when the brine is flashed.

In August we wrote to 16 leading companies in the fields of water treatment, including firms dealing with oil-field and boiler scales, some having previous experience with geothermal systems, and others offering lines of corrosion inhibitors as well as scale inhibitors. Complete data on the temperatures and chemical composition of the brine, and the general chemical compositions of the scales were furnished in the letters. Replies were received from nine of these companies, of which seven offered at least one additive for testing. All of the industrial contacts have noted the severity of this problem: the high temperatures involved, the high salt concentration, and the lack of knowledge of the behavior of silica under these conditions. Although a number of additives were proposed, the tone was generally pessimistic.

Three companies that did not reply initially were contacted again, and one (Tretolite) offered its product for testing. However, because this product was chemically similar to several found in the course of testing to be marginally effective, this material was temporarily set aside in favor of an additive that was chemically different and was reputed to act in a way different from the other substances. The final group of proprietary scale control additives thus comprised eight products. These are listed in Table 1.

Table 1. Proprietary Additives Tested in November - December, 1978 Test Series

Product Name	Company, Address	Chemical Type	Concentration Tested, ppm
Geomate 256	Dearborn Chemical Corp., Lake Zurich, IL	Phosphonate + Polymer	35
CL-165	Calgon Corp., Pittsburgh, PA	Polymer mixture	18
Drewsperse 747	Drew Chemical Corp., Boonton, NJ	Phosphonate + Polymer	15
Betz 419	Betz Laboratories, Trevose, PA	Phosphonate + acrylic Polymer	20
Thermosol APS	Far-Best Corporation, Los Angeles, CA	Polyalkylphosphonate	20
S-404	C-E Natco, Bakersfield, CA	Organic Polymer	18
SC-210	Southwest Specialty Chemicals, Houston, TX	Low molecular weight carboxylic acid	10
Cortron R-16	Champion Chemicals, Anaheim, CA	Filming amine	120, 20

Because of severe restrictions on the time available for field testing, we hoped through some preliminary testing to develop a screening method that would permit a more rapid differentiation of the effects of the various additives. However, no sufficiently reliable and valid method was found (some aspects of this will be discussed in detail below); thus the decision was made to test each candidate additive for a period of approximately 70 hours at a single concentration. The concentrations to be used were decided upon in consultation with the manufacturers of the products, and generally were the maximum cost-effective concentrations likely to show a beneficial effect, with consideration being given also to the dangers of overfeeding some of these materials.

In the case of most of the proprietary scale-control additives, we did not know the exact chemical composition of the mixtures and hence the hazards involved in their use. Thus a prerequisite for testing an additive was that the company furnish us with a completed Materials Safety Data Sheet for their product.

In addition to 3-day tests of each of eight proprietary additives, the test series also included two control runs, a 4-1/2 day test of Natrosol 250LR at 18 ppm, a 23-hour test of the addition of geothermal sludge as a seeding agent to retard scale, a test of a commercial magnetic water conditioner for scale reduction, an attempt to measure the rates of scale accumulation as a function of time, and a test of a packed column for the rapid measurement of brine scaling tendency.

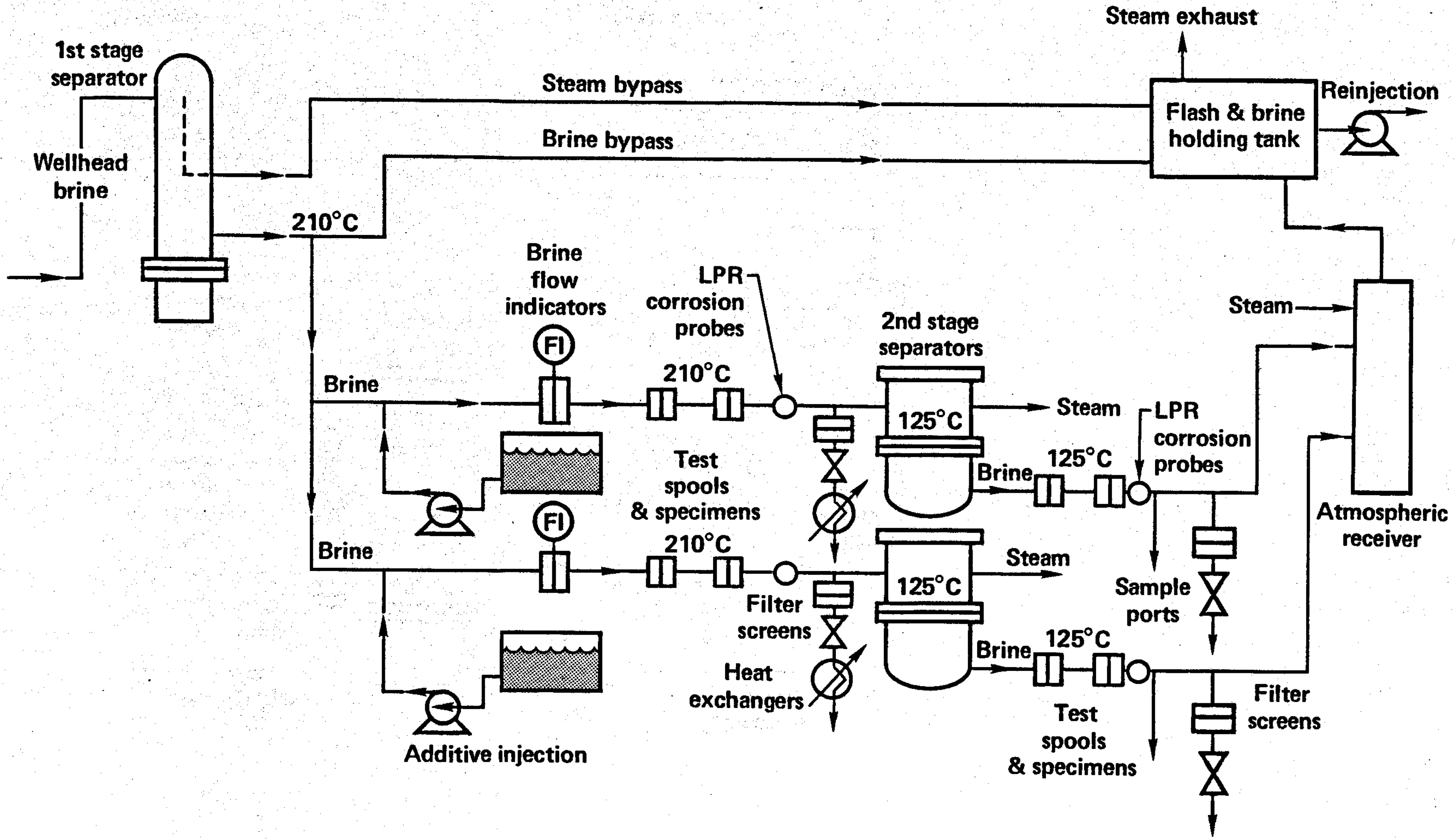
Brine Scaling Test Apparatus

The system constructed for flashing the brine and measuring the scaling tendency of treated brine is shown schematically in Figure 1. In this apparatus two-phase fluid from Magmamax No. 1 well was first passed through a C-E Natco wellhead separator of the centrifugal type. The steam was discarded and single-phase brine was thus obtained at nearly wellhead temperature (200-220°C) and pressure (290-320 psia). The brine was then divided into two nominally identical channels for the testing of the scale control additives. These are designated channels A and B.

The brine in each channel was flashed from ~210°C temperature to 125°C in flash vessels and then passed to an atmospheric receiver. The pressure at the exit of the 125°C flash vessels was about 15 psig. Brine flow was maintained in each channel at 7.0 gpm (~1 lb/sec) by monitoring the pressure drop (~15 in. H_2O) across an orifice plate that was cleaned periodically. Additive solution (at about 0.5-1.0% strength) was metered into the brine using high pressure pumps equipped with pulsation dampeners, and this flow was monitored and maintained at 0.030 gpm by means of Flow Technology turbine flow meters. All of the piping in the test sections of the system were 1-inch i.d. except where the corrosion probes were mounted. The additive solution was introduced into the flowing brine through a concentric 1/4-inch o.d. tube, approximately eight feet upstream of the first test specimen. During each experimental run, all of the pertinent pressures, temperatures, and flows were monitored and recorded continually.

FIGURE 1

SCALE-CONTROL TEST SYSTEM



Measurements of Brine Characteristics

During each test run, the scaling and corrosion characteristics of the brine were measured by several different techniques, and each was applied at the two basic temperatures of the test -- 210 and 125°C. The removable test specimens were as follows:

- Test Pipe Spools. Twenty-four-inch-long sections of 1-inch i.d. mild steel pipe, flanged at each end. These were cut in cross section for measurement of the thickness of accumulated scale.
- Mild Steel Test Coupons. A pair of 1.25 X 0.5 X 0.025-inch coupons of AISI 1009 steel mounted on a holder, and placed in the downstream flange of the test spools so that the brine flow was parallel to the long dimension of the coupon. The weight gain and the increase in thickness of the coupons after exposure were measured to provide an indication of the combined effects of scaling and corrosion.
- Inert Test Coupons. These were designed 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-inch pieces of TFE Teflon and Hastelloy C-276 and were mounted on the Petrolite corrosion probe assemblies. Because these assemblies were located in 2-inch i.d. pipe sections, the inert coupons were subjected to a lower velocity of brine flow than the mild steel coupons.

- Petrolite Corrosion Probes. Type 510 three-electrode probes fitted with AISI 1018 mild steel electrodes, for measurement of corrosion rates by the linear polarization resistance (LPR) technique. The probes were connected to Petrolite Model M-3010 automatic recording instruments for continuous monitoring of the corrosion rates.
- 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 210°C brine (see Figure 1) 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. Flow of brine through the screens was controlled at 0.75-1.0 liters/min by adjustment of downstream valves so that the mainstream temperature was maintained across the filter holder. The temperatures at the outputs of the screens in the 210°C brine were monitored by means of thermocouples. Severe plugging of the screens was indicated by an inability to maintain the flow rate, and/or a decrease in screen output brine temperature. After flow through the screen and output valve, the 210°C brine was quenched to ambient temperature in a cooling-water heat exchanger. The scaling tendency of the brine was indicated by the visual appearance and weight gain of the screens during exposure.

Several chemical tests were also carried out during each test run:

- The gross chemical composition of the effluent brine was monitored at least daily by determination of its pH, density, and its concentrations of chloride and silica.
- The turbidity, and its increase with time, of the brine quenched from the 210°C sidestreams was measured with a Hach Model 2100A turbidimeter. This provided an approximate measure of the brine particulate level and, it was hoped, some indication of the integrity of the additives at high temperature.
- The stability of the brine with respect to the precipitation of silica was determined by collecting effluent brine, incubating it anaerobically at 90°C, and performing our "standard" filtration tests[4] on it at intervals of 15 and 30 minutes.

Additional chemical analyses conducted to characterize these tests were (a) complete analysis of several samples of brine taken from the wellhead separator, and (b) analyses of the scales, primarily those from the Teflon specimens, which will provide information on the interactions between the additives and specific constituents of the brine.

Results and Discussion

Initial Test Run. The first experimental scale-control run of the November/December test series was designed to be an extended test of the performance of Natrosol 250LR and to provide untreated brine for experimentation with several scaling-rate measurement methods. The characteristics of the brine during this and the subsequent runs are listed in Table 2 (Run 7 is a continuation of the numbering system begun in July). The data of Table 2 show that the composition of the brine was remarkably constant during the entire test period; with the exception of 14 November, the GLEF was operating continuously at two-thirds to full flow during this time.

In the initial test run, untreated brine was flowed in Channel B of the test system and a concentration of 18 ppm Natrosol 250LR was maintained in Channel A.* The total duration of the run was 113 hours. During this time, brine at both 210 and 125°C was flowed from each channel through sections of 1/4 and 1/2-inch o.d. mild steel tubing which were removed at intervals. The results of these exposures are not yet available, but they should yield a measure of the variation, if any, of the rates of scaling as the test run progressed. The 1-inch pipe spools that were exposed during each run also have not, at this writing, been examined in detail. The accumulation of scale on the other types of specimens has been measured, and these results for all of the additives tested will be summarized below.

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* Additives were metered to provide the nominal concentration at the high-temperature point of addition. This concentration increased ~15% after the second-stage flash because of the steam loss.

Table 2. Characteristics of Effluent Brine at LLL Plant During Proprietary Additive Tests

	Date	Time	SiO_2, mg/kg	Chloride M/ℓ	Density at 25°C g/cm^3	pH
	11 Nov	1200	453	4.00	1.157	-
Run 7	12 Nov	1615	462/481	4.02	1.157	-
	13 Nov	0900	461	3.98	1.160	-
	14 Nov	1500	458	3.60	1.145	-
	15 Nov	0930	484	3.90	1.150	-
	15 Nov	1500	490	4.00	1.156	-
	16 Nov	1400	471	4.00	1.159	-
	17 Nov	0730	481	4.00	1.157	5.89
Run 8	18 Nov	1430	454/448	4.00	1.155	5.80
	19 Nov	0944	443	4.10	1.159	5.83
	20 Nov	1425	425	4.00	1.157	-
	21 Nov	0800	429	4.00	1.158	5.92
Run 9	2 Dec	1400	480	4.02	1.157	5.80
	3 Dec	1107	467	4.00	1.158	5.80
	4 Dec	1330	456	4.00	1.163	5.92
	5 Dec	0815	473	4.01	1.163	5.96
	6 Dec	No Analysis				
Run 10	7 Dec	1350	464	4.02	1.162	5.83
	8 Dec	1330	470	4.00	1.160	5.88
	9 Dec	0815	460	4.05	1.161	5.72
Run 11	10 Dec	0830	470	4.05	1.161	5.94
	11 Dec	0845	470/466	4.06	1.161	5.97
	12 Dec	0830	461	4.06	1.161	5.89
Run 12	13 Dec	0935	460	4.10	1.162	5.73
	14 Dec	1040,1555	516/504	4.07	1.162	5.87
	15 Dec	0830	469	4.12	1.163	5.83

Tests of Packed Metal-Ball Column. Any technique that could be developed for rapidly measuring the scaling tendency of a geothermal brine would greatly speed the screening of potential additives for scale inhibition. One such approach is to present to the flowing brine a large surface area for contact; then presumably, if significant scaling occurs, there would be a measurable decrease in concentration, in the brine, of the principal constituent of the scale.

We attempted to implement this idea in the form of a packed column of mild-steel spheres, with a measurement of the silica in the brine both before and after passage through the column.

The column was 1-inch i.d. by 8-inch long and was packed with 1/16-inch diam. carbon steel balls. It was calculated that at a flow rate of 1 liter/sec and a scaling rate of 1 mil/hr, the brine passing through the column should decrease in silica concentration by 180 mg/kg. Several tests of the column at 125°C, however, resulted in no detectable change in the brine silica concentration. This test was not necessarily definitive because the scaling rate of the brine was much less than anticipated -- 0.1 to 0.2 mil/hr, most of the scaling appeared to take place at the top of the column, and there may have been some channeling through the column.

Test of Magnetic Water Conditioner. Although the mechanism is not completely understood, some authors have reported that exposure of scaling fluids to magnetic fields reduces their scaling tendencies[6], and some equipment is available commercially for water treatment by this technique. We have tested one such unit, a so-called "Water Conditioner", manufactured by the Superior Company of Ft. Wayne, Indiana, Model C-100, having a capicity of 1 gpm. It was connected to the sample ports at 125°C, and brine was flowed through it at 1 liter/min. The scaling tendency of the effluent brine was to be measured by means of a perforated screen and compared to that of the input brine. Unfortunately, the water conditioner completely plugged after less than one hour of operation. The unit is a cylindrical tubing assembly with pipe connections on each end. When we disassembled the unit that failed, we found that internally, it was constructed in large part of copper, which corroded badly, and the fluid was constrained to flow through some very small orifices which plugged with scale. Thus, although this product certainly could not be used without modification for geothermal brines, it did not provide a definitive test of the concept of brine magnetization for scale control.

<u>Scaling Rates of Additive-Treated Brines</u>. Table 3 summarizes the results of the measurements of the rates of scaling of the three types of test coupons at 210 and 125°C for all of the brine additives tested in the November/December series. The data are listed in the chronological order in which they were obtained; after the inital run, a pair of additives was tested together, one in each channel of the system. The total thickness of scale accumulated on the coupons was measured by means of a micrometer and divided by two to give the single-side totals listed in Table 3. Data are missing for the following reasons: the Teflon coupon in the Natrosol run became dislodged from its mounting; some of the Hastelloy coupons exhibited quite flakey, non-adherent scale, preventing accurate thickness measurement; and adherent scale could not be separated from accumulated sludge on the low temperature Teflon and Hastelloy coupons in the seeding experiment.

In general the weight gains of the coupons paralleled the increases in thickness, and data for the duplicate mild-steel coupons of a given run were in close agreement. The variation of the thickness of the scale over the surface of a coupon was usually within 0.5 mil at 210°C and 1 mil at 125°C. For a given brine treatment, the differences in scaling rates for the three materials are significant and reflect (a) the differing surface chemical reactions that affect the growth of the scale and (b) differences in fluid flow at the surfaces. Quite a variety of colors and textures of the scales were found in these tests; chemical analyses of the scales will be a great aid in deducing the exact nature of these observations.

Table 3. Scaling Rates of Brines Containing Various Additives

			Scaling Rate Scale Thickness (mils) and Scaling Rate (mils/hr)											
			210 °C						125 °C					
			Mild Steel		Hastelloy		Teflon		Mild Steel		Hastelloy		Teflon	
Channel	Additive	Time of Exposure, hr.	Total	Rate	Total	Rate	Total	Rate	Total	Rate	Total	Rate	Total	Rate
A	Natrosol 250LR	113	0.5	0.005	0.5	0.005	-	-	17	0.15	10	0.09	15	0.13
B	None-Control B	113	2	0.02	1	0.01	5	0.05	24	0.21	11	0.10	12	0.11
A	Geomate 256	69	8	0.10	2	0.03	4	0.05	18	0.26	30	0.43	31	0.44
B	Calgon CL-165	69	10	0.15	-	-	21	0.30	10	0.14	17	0.25	23	0.33
A	Drewsperse 747	69	8	0.10	11	0.16	10	0.14	9	0.13	5	0.07	7	0.10
B	Betz 419	69	3	0.04	-	-	4	0.06	8	0.10	22	0.31	21	0.30
A	Thermosol APS	64	4	0.06	-	-	5	0.08	12	0.19	6	0.09	8	0.13
B	Natco S-404	64	12	0.20	12	0.20	5	0.08	19	0.30	7	0.11	8	0.13
A	SW Chem SC-210	66	10	0.15	-	-	7	0.11	15	0.22	3	0.05	5	0.08
B	Cortron R-16	66	8	0.12	4	0.06	4	0.06	55	0.83[a]	24	0.36[a]	25	0.38
A	None-Control A	65	5	0.08	1	0.02	2	0.03	25	0.38	4	0.06	6	0.09
B	Sludge	23	1	0.04	4	0.17	5	0.20	29	1.3	-	-	-	-

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[a] Plant upset caused higher rates;
see text

Firm conclusions must await these chemical analyses and measurements of the scale on the pipe spools; nevertheless, several other facts have emerged from the data of Table 3. First it is apparent that the scaling rate of untreated brine at 125°C was considerably less than that expected from previous LLL Four-Stage Flash System and GLEF tests. For mild steel, the scaling rate was a factor of 3 to 5 less than the 1 mil/hour rate previously observed at lower temperatures. The lower scaling rate may be due partly to the ~20% decrease in the salinity and silica content of the brine from the levels existing during prior operations. Second, these data indicate that neither Natrosol, nor any of the proprietary additives had a very large effect on the scaling rates at 210 or 125°C. Comparison of some of the scaling rates with those for untreated brine could lead one to believe that some of the additives under certain conditions did greatly reduce the scaling rates. However, the data of Table 3 must be considered in light of our discovery that the inherent scaling rate of the brines in the two channels of our system were not identical, and may not have been perfectly constant during the course of the whole test series. This was most evident in tests with the perforated screens.

In most of the measurements with the screens, the standard test was to flow brine through the high temperature screen for 48 hours and through the low temperature screen for 24 hours. A difference in channels became evident during the proprietary additive runs, and this was confirmed during the final run in a 24-hour test in which a screen was exposed in each channel, simultaneously, at 125°C. It was found that the scaling tendency of the brine, for this particular measurement technique, was much less in Channel A than in Channel B. The reason for this difference is not known, and a lengthy discussion is beyond the scope of this report; however, it was observed that the particulate level was generally higher in Channel B, especially leading to more rapid plugging of its high temperature screen. This difference in system channels means that data for a particular additive should probably be compared to that for untreated brine obtained in the same channel, but this still assumes constant day-to-day brine conditions. For example, restricting our attention to the scaling rates at 125°C on the mild steel coupons, and comparing data for individual channels, we would conclude that additives deserving further attention (greater than a factor of two reduction in scaling rate) are Natrosol, Drewsperse 747, and Betz 419. However, these recommendations are tentative until all of the test results have been compiled.

The result for the sludge seeding experiment was inconclusive and will be discussed below. The result for the Cortron R-16 deserves further discussion. This additive was different from the others because it is a filming amine, designed to coat metal surfaces, preventing their corrosion and the adherence of scale, rather than inhibiting the growth of scale per se. During the test run with this additive, there was a period of malfunction that caused the second-stage flash vessel to operate at a higher liquid level. This caused a longer brine residence time in this channel at 125°C, and this probably accounts for the much greater accumulation of scale on the 125°C coupons. The Cortron R-16 was not effective in inhibiting this scale or the scale formed at 210°C, and it also did not reduce the corrosion rates (see below); however, the low temperature scale that formed on the inert coupons and Petrolite assembly was quite powdery and easily removed, thus it may still have some promise as an additive.

<u>Results of Incubation Tests</u>. One of the routes to finding an agent that will inhibit the formation of silica-rich scales is finding a chemical that will retard the rate of polymerization of silica in brine that is supersaturated in silica. Incubation of supersaturated brine at 90°C and measurement of the rate of silica precipitation has been developed [4,5] as a method for screening potential additives. The premise is that a substance that decreases the rate of precipitation of silica in solution also will have the potential for decreasing the rate of growth of silica on the surface of forming scale. However, the fact that a substance is effective

at 90°C does not necessarily mean that it will be effective at higher temperatures. Indeed, the types of compounds that operate as colloid stabilizers in situations such as this probably will be less effective as the temperature is raised, primarily because most of them are polymers that have inverse temperature coefficients of solubility. By the same token it is unlikely that there is an additive that would be potent as an inhibitor at high temperature, but which would not be revealed as effective at lower temperatures where the rate of silica precipitation is greater. Our hope is that the 90°C incubation test is valid insofar as the results are related to the scaling rates at that temperature, and that the diminished effect of inhibition at higher temperatures will not be greater than the decrease in scaling rates.

The incubation test consists of collecting brine from the 125°C sample ports, holding the brine at 90°C out of contact with air, and then measuring the concentrations of precipitated solids and silica (<1 μm particle size) remaining in solution at timed intervals after sampling. For times up to ~4 hr, the brine is contained in screw-cap bottles with Viton gaskets; for longer times, the brine is sealed in glass ampoules under high-purity nitrogen. In Figure 2 are curves showing the rates of solids and silica precipitation for the brine of the November/December test series, to which no chemicals were added.

Table 4 summarizes the results of the incubation tests performed on the treated brines of the November/December test series. These data show that only Natrosol has a significant effect on the rate of silica precipitation. Thus far, of the substances we have tested by addition in the plant at 210°C, only Natrosol and the Ethomeens (in the July test series) have shown activity toward silica.

FIGURE 2. Rates of Formation of Solids and Precipitation of Silica from Geothermal Brine at 90°C. Brine pH = 5.7 and 4.1 M/ℓ Chloride.

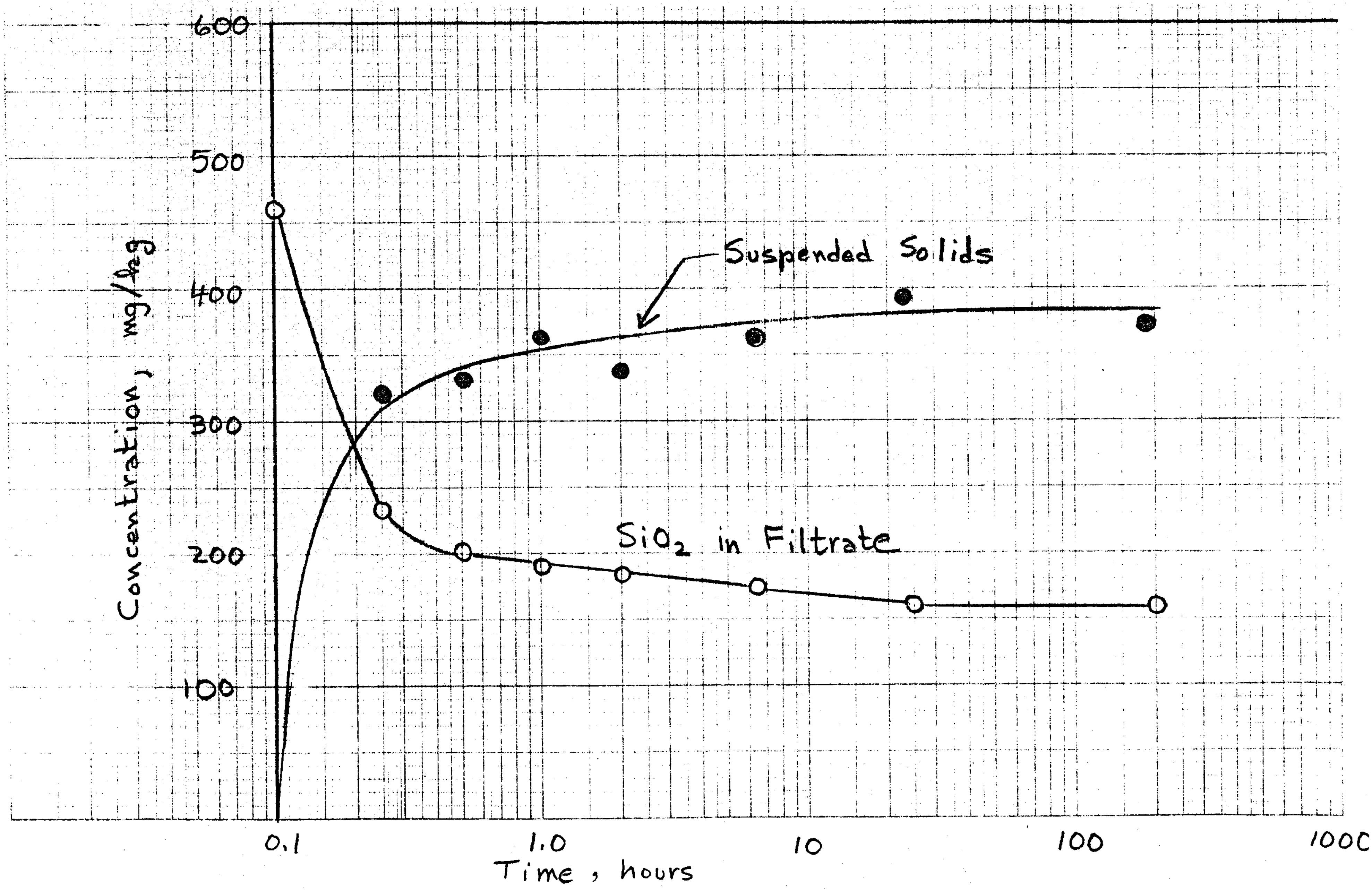

Table 4. Rates of Precipitation of Solids and Silica from Effluent Brine (90°C) Containing Various Additives. Concentrations in mg/kg.

	No Additive, Control B		No Additive, Control A		Hercules Natrosol 250LR		Geomate 256		Calgon CL-165		Drewsperse 747		Betz 419	
Incubation Time, min.	Solids	Filtrate SiO_2	Solids	Filtrate SiO_2	Solids	Filtrate SiO_2	Solids	Filtrate SiO_2	Solids	Filtrate SiO_2	Solids	Filtrate SiO_2	Solids	Filtrate SiO_2
0	-	481	-	460	-	462	-	454	-	448	-	467	-	467
15	272	264	321	236	77	447	266	241	289	222	256	271	303	246
30	298	213	331	203	103	388	304	191	309	213	299	212	311	203

	Far-Best Thermosol APS		C-E Natco S-404		SW Chem SC-210		Champion Cortron R-16	
Incubation Time, min.	Solids	Filtrate SiO_2	Solids	Filtrate SiO_2	Solids	Filtrate SiO_2	Solids	Filtrate SiO_2
0	-	464	-	473	-	470	-	466
15	273	252	266	252	312	252	270	247
30	309	184	301	199	326	203	302	206

It should be noted that deposit inhibitors which operate to decrease scale adherence would not be expected to show retardation of silica precipitation. Thus the incubation test is not regarded as valid for all approaches to scale control, but for all of the proprietary additives except Cortron R-16, the incubation test tended to corroborate their small effect on the scaling rates. We note that in the case of the results for Natrosol, good performance in the incubation test may be a necessary -- but not a sufficient condition -- for reduction of scale.

Chemical Analyses of Scales. One of the keys to understanding the effects, if any, of the additives on the reactions that form scale are the chemical analyses of these deposits. Table 5 lists the analyses obtained for four of the low-temperature scales deposited on the Teflon coupons. The full significance of these data is not yet known but it is interesting that (a) Natrosol significantly decreases the concentration of silica, and increases the concentrations of iron and manganese in the scale, and (b) the scale obtained in the presence of the Geomate 256 was pure white and contained virtually none of the metal sulfides common to the other scales. Analyses of the scales formed in the presence of the other additives are in progress.

Table 5. Chemical Composition of Scales Deposited at 125°C on Teflon Coupons

	Concentration wt%			
Element	Control B	Natrosol 250LR	Geomate 256	Calgon CL-165
SiO_2	83	60	88	83
S	0.3	0.3	0.0	0.2
Cl	0.08	0.4	1.1	0.4
K	0.8	0.8	0.3	0.4
Ca	0.45	0.56	0.80	0.56
Cr	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
Mn	0.20	1.2	0.16	0.17
Fe	1.1	5.5	0.56	1.2
Cu	0.59	0.57	0.04	0.25
Zn	0.13	0.21	0.08	0.14
Ga	0.01	≤ 0.01	0.01	0.01
As	0.03	0.1	-	0.02
Br	-	-	0.003	-
Rb	0.01	0.01	0.005	0.006
Sr	0.006	0.008	0.012	0.008
Y	≤ 0.01	≤ 0.01	-	-
Ag	0.03	0.07	≤ 0.02	0.05
Sb	≤ 0.03	0.03	≤ 0.2	≤ 0.1
Ba	0.05	0.08	≤ 0.05	0.01
Pb	0.21	0.33	0.02	0.16
Ni	≤ 0.002	-	-	-

Electrochemical Corrosion Measurements. Table 6 summarizes the data on the corrosion rates of the brines measured by means of the linear polarization resistance technique. The values listed are the levels obtained after about 12-hr of specimen exposure and in all cases these values held nearly steady for the durations of the exposures. It is striking that the corrosion rates at 125°C for the untreated brines, and several of the treated brines, were higher than the rates at 210°C. This must reflect the relative degrees of protection afforded by the corrosion films and scales formed at these temperatures. The higher corrosion rate at 125°C in the brine with the Southwest Chemical SC-210, coupled with its low scaling rate at this temperature (see Table 3) suggests that it may have exhibited some scale inhibition. The higher corrosion rate in the presence of the Cortron R-16 may be a result of the greater porosity of its scale. It should be realized that complete scale inhibition may result in much higher corrosion rates than are usually observed for scaling brines.

Table 6. Steady-State Corrosion Rates of Mild Steel AISI (1018) in Additive-Treated Brine Measured by Linear Polarization Resistance Technique

Additive	Corrosion Rate, mpy		Remarks
	210°C	125°C	
None-Control B	7	15	
Natrosol 250LR	6	-	Debris on electrodes prevented low temp reading
Geomate 256	3	15	
Calgon CL-165	5	2	
Drewsperse 747	7	15	
Betz 419	7	4	
Thermosol APS	7	5	
Natco S-404	5	3	
SW Chem SC-210	5	25-60	Low Temp. readings erratic at first; steady >48 h
Cortron R-16	7	25	
None-Control A	9	14	
Sludge	10	14	

Seeding Experiment. Another approach to scale control that has been attempted by other investigators (see, for example, Reference 7) is to add to the fluid a finely divided solid upon which the scale-forming compound deposits in preference to the plant surfaces. The rationale is similar to the addition of seed crystals to promote precipitation in crystallization processes. Although the scale with which we are dealing is predominantly amorphous silica, by providing a large ratio of seed-to-plant-surface area, reduction of the degree of supersaturation and hence the scaling tendency of the brine should be attainable. Also, to be a viable technique, the seed substance must remain fluidized and pass through the plant equipment with minimal holdup.

For Salton Sea geothermal brines the ideal seed material would be colloidal silica. Closely approaching such material is the wet sludge obtained from the sedimentation of the effluent brine from the GLEF prior to injection. This sludge is of mud-like consistency and is a finely-divided precipitate composed primarily of silica, with lesser amounts of iron compounds and metal sulfides, i.e., all of the usual ingredients of geothermal scale. Using sludge as a seed material appeared promising because earlier work[8] on developing an effluent process for this brine demonstrated the effectiveness of pre-precipitation solids contact as a means of rapidly promoting the precipitation of silica.

A short experiment of seeding for scale control was conducted during the November/December series as a prelude to a longer-duration, more extensive test. In this experiment a suspension of wet sludge containing 20% by weight solids was metered into the 210°C brine in the same manner as the chemical additives. This sludge contained, in addition to the compounds mentioned above, small amounts of $BaSO_4$ and $CaSO_4$; these were present because of the addition of Salton Sea water in the pilot clarifier tests conducted by the Imperial Magma Company. After an initial short period without additive flow to establish brine silica levels, the sludge feed rate was controlled for one hour at 0.30 gpm and then for 22 h at 0.15 gpm. At 0.15 gpm, assuming 10 μm spherical seed particles and a 1-in. i.d. pipe diameter, a 10:1 particle-to-pipe surface area ratio is obtained.

Since the usual chemical feed pumps cannot be used for slurries, a Moyno progressive-cavity type pump was used for pumping the sludge, and for this short test no difficulties were experienced. Sludge flow rate was measured manually by a volume displacement technique.

In the measurement of scaling rate it was found that screens could not be used because they were rapidly plugged by the accumulation of the suspended sludge. A screen at the 125°C brine sample port plugged in less than an hour. Similarly, there was an accumulation of sludge on the test coupons, especially at corners and attachment points, making it difficult to distinguish scale from sludge deposits. The data of Table 3 represent our best estimates of the thickness of the deposits on the coupons. The Petrolite probe in 125°C brine was so heavily covered with sludge that no estimates of either scale thickness or possible erosion on the Teflon or Hastelloy coupons could be made. Compared to the "B" control channel, it appears that sludge addition does not reduce scaling; however, examination of the test spools and a longer-duration test must be completed before a final judgement can be made.

A superior measurement method for detecting the effect of seeding may lie in our measurements of the levels of silica in the brine during the experiment. These data, shown in Table 7, were obtained, with one exception, as follows. The test brine (quite dark colored in appearance) was flowed dropwise onto a filter crucible connected to a vacuum flask in such a manner that a minimum time of contact with the sludge filter cake was obtained. Hydrochloric acid was placed in the filter flask to immediately acidify the filtrate and prevent further precipitation of the silica. The silica in the filtrate was determined by atomic absorption spectrophotometry. Using this technique it was found that (see Table 7) seeding reduced the level of dissolved (particle size <1 μm) silica from 453 to 431 and 416 mg/kg at 210°C, which is probably not a significant change, but from 516 to 306 mg/kg at 125°C, which is a substantial reduction in the degree of supersaturation.

This measurement technique, however, may not be completely valid. Because of the extremely rapid reaction of dissolved silica with the seed silica at low temperatures, it is possible that some of the decrease in the concentration of silica occurred as the brine was being filtered. Thus an additional experiment was tried in which the brine at 125°C was captured first in acid and then filtered. This yielded the value of 396 mg/kg, higher than before, but still significantly lower than the starting value of 516 mg/kg.

Table 7. Measurements of Concentration of "Dissolved" Silica in Brine during the Seeding experiment. Concentrations of SiO_2 in mg/kg

210°C

Before Sludge Addition	After Sludge Addition 0.3 gpm	After Sludge Addition 0.15 gpm
453	431	416

125°C

Before Sludge Addition	After Sludge Addition 0.3 gpm	After Sludge Addition 0.15 gpm	After Sludge Addition 0.15 gpm 2[a]
516	306	306	396

[a] Immediate acidification of sludge-containing brine.

From these limited data it appears that (a) the reduction in dissolved silica at low temperature (125°C) is sufficient to warrant further tests, (b) a still lower concentration of sludge than used here might be just as effective, (c) some different test surface configurations may have to be devised to measure scaling rates in the presence of sludge, and (d) on the basis of the corrosion data in Table 6, seeding does not increase the general corrosion rates.

In this relatively short duration experiment, several inches of sludge accumulated in the bottom of the second stage separator, indicating that process equipment may require special design features to accommodate sludge injection as a means of scale control.

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