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UCID-18521

Final Report on Tests of Proprietary
Chemical Additives as Antiscalants for
Hypersaline Geothermal Brine

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MASTER

January 1980

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Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.

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CHEMICAL ADDITIVES AS ANTISCALANTS FOR
HYPERSALINE GEOTHERMAL BRINE

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Abstract

The Lawrence Livermore Laboratory brine treatment test system has been used to carry out a short-term evaluation of a number of proprietary chemical additives as antiscalants for the hypersaline brine of the Salton Sea Geothermal Field. In addition, we conducted a test of sludge seeding as a technique for scale control. The effect of each additive on the rate of precipitation of silica from the effluent brine at 90°C was measured, and scaling rates of brine treated with nine of the additives were measured at 125 and 210°C. Corrosion rates of mild steel in the treated brines were estimated using Petrolite linear polarization resistance equipment. None of the additives had a direct effect on the rates of silica precipitation, and none had a beneficial effect on the scale formed at 210°C. At 125°C, two additives, Drewspers 747 (Drew Chemical) and SC-210 (Southwest Specialty Chemicals) afforded a marginal degree of scale reduction. The Austral-Erwin additive diminished the adherence of scale formed at points of high velocity fluid flow but increased solids accumulation at other points. Sludge seeding shows some promise because it reduces the degree of silica supersaturation of the brine. Results of analyses of solids precipitated from effluent brines (Woolsey No. 1 and acidified Magmamax No. 1) are presented.

Introduction

This report constitutes a final summary of the results of tests of proprietary additives for geothermal scale control that were carried out during fiscal year 1979. To distinguish these tests from others that we have conducted using other chemicals, we have defined proprietary additives as those brand-named, commercial compounds or mixtures of compounds whose identities are a trade secret. As a result of an industry-wide solicitation, a group of eight such additives were submitted to us for test

early in the year, and a preliminary description of those results has been published.¹ Sludge seeding was also tested briefly as a scale control technique.¹ Later in the year we examined the Austral-Erwin additive in a scaling test, and evaluated eight additional proprietary chemicals as inhibitors for silica precipitation.

A parallel investigation was the evaluation of other types of compounds--also brand-named, commercial chemicals available in bulk--but with identities known to us, so that, hopefully, we could develop an understanding of the classes of substances that might be active toward silica in geothermal brine. The results of these tests of organic additives are reported in another series of publications.²⁻⁶

A major emphasis in our work has been to develop and use techniques of scaling rate measurement that would minimize the time required to evaluate a single additive, yet still provide useful information for prediction of performance in larger facilities and for longer times. Several techniques for obtaining a faster indication of brine scaling tendency were examined in the course of this study, and general comments on their performance will be given.

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.

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

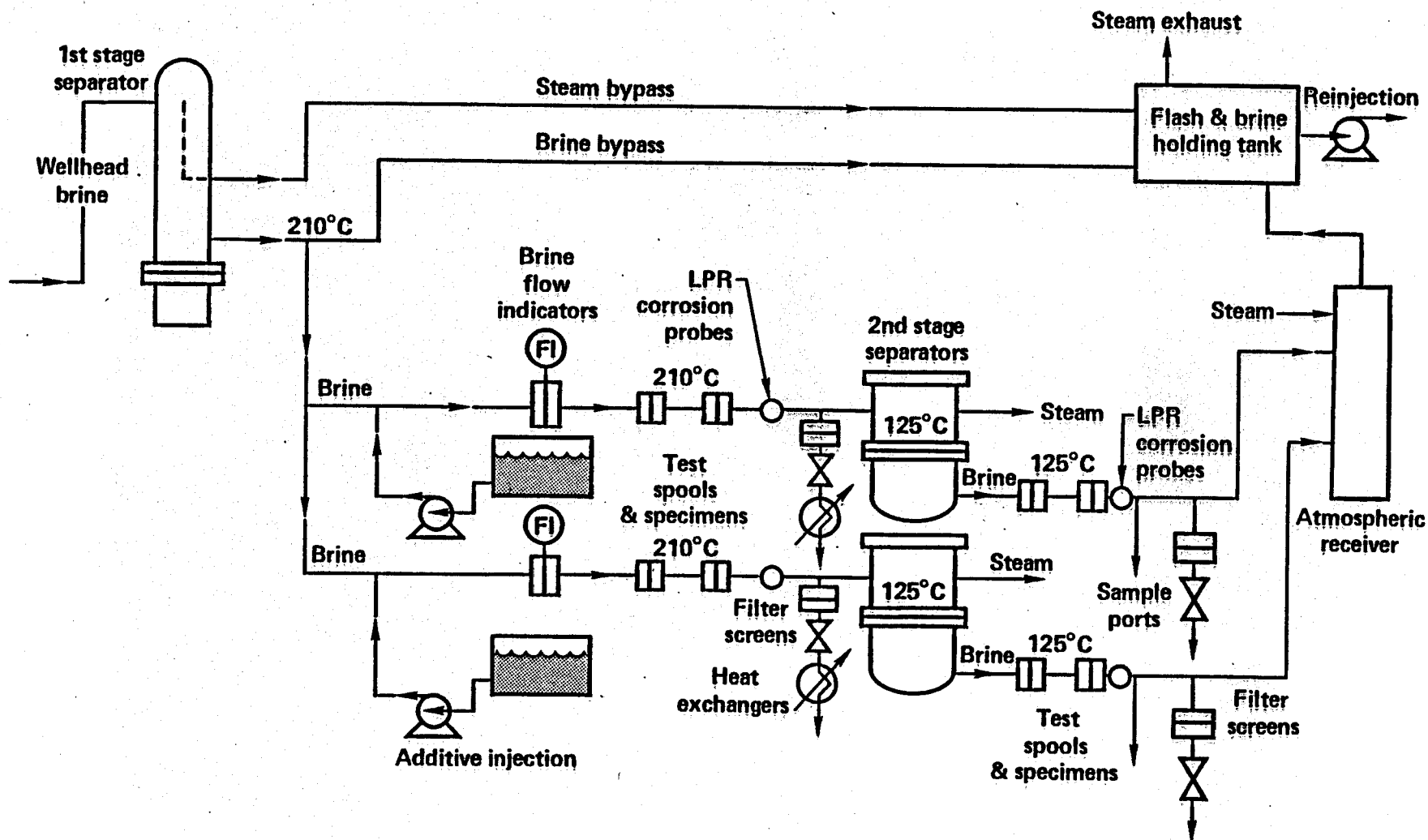
pressure drop (~ 15 in. H_2O) across an orifice plate that was cleaned periodically. Additive solution (at about 0.5-1.0% strength) was metered into the brine using high pressure pumps equipped with pulsation dampeners, and this flow was monitored and maintained at a point in the range 0.020-0.040 gpm 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 coaxial 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. The accuracy of maintaining a desired concentration of additive was determined in a tracer study using cesium ion and found to be $\pm 10\%$.

Measurements of Brine Characteristics

During each scaling 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, potted with epoxy, and polished 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.

FIGURE 1
SCALE-CONTROL TEST SYSTEM



- 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. Neither Teflon TFE⁷ nor Hastelloy C-276⁸ are attacked at an appreciable rate by the hypersaline brine. 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 estimation 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 0.5-1.0 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.

In the precipitation test,⁹ the additives are injected into the brine at $\sim 210^{\circ}\text{C}$ as described above, and the brine samples are collected for study from the 125°C sampling ports. During sampling, the brine flashes to 105°C . It is then placed in air-tight, Viton-gasketed, 130-ml, screw-cap glass bottles and incubated at 90°C . For incubations longer than 2 h, sealed glass ampoules are used.⁹ At appropriate intervals after sampling, the bottles are opened and the contents filtered through fine-porosity glass crucibles. The silica remaining in the filtrate is measured by atomic absorption spectrophotometry using the method of standard additions. Measurement of the silica in this manner has been shown to yield values for the total concentration of silica (monomeric, polymeric, and particulates $<1\ \mu\text{m}$ in size) not retained by the filter. The initial concentration of silica in the brine sampled at the effluent port was determined in samples immediately acidified with hydrochloric acid. The collected solids are dried in air at 105°C and weighed as a measure of the suspended solids concentration of the brine.

The precipitation test is used to determine whether a candidate additive inhibits the precipitation of silica from the brine at 90°C . Activity as a precipitation inhibitor is a prerequisite for antiscaling activity by the colloid stabilization mechanism, and we have used this test as a method for screening organic compounds as potential antiscalants.²⁻⁶ At the 90°C temperature of the test, good correlations have been found between precipitation inhibition and scale reduction. However, it is recognized that colloid stabilization is not the only mechanism that may be viable here. Thus for the initial group of eight candidate additives, measurement of their effects on the scaling tendency of the brine was regarded as mandatory and the only definitive test.

Chemical Analyses of the Brines

As usual, the major parameters of the brine (pH, density, chloride, and silica concentrations) were monitored continually during the proprietary and generic chemical additive experiments. There is evidence, described in detail elsewhere⁶ that from June, 1978, until June, 1979, the brine at full well flow ($\sim 600\ \text{gpm}$) was less saline than normal, i.e., $\sim 4.0\text{--}4.1\ \text{mol/l}$ chloride, compared to previous levels of $\sim 4.5\ \text{mol/l}$.

More complete analyses of the brine were occasionally performed using atomic absorption spectrophotometry, inductively-coupled-plasma emission spectrometry, and a gravimetric method for sulfate. As in the past, the concentrations of sodium, potassium, calcium, and the minor constituents paralleled the measured levels of chloride, and no significant relative changes were noted.

Observations on Testing Techniques

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. In the tests of the various additives we have made the following observations on the testing techniques:

1. Use of a packed metal-ball column was unsatisfactory, probably because of the difficulty in providing a large surface area for brine contact throughout the columns. However, successful experiments of this type using simulated geothermal brines and other packing materials have been done recently at Oak Ridge,¹⁰ and additional work could be done to optimize the metal column used here. However, as discussed below, apparatus such as this, which depends on passing the brine through small orifices with a large surface area of contact, is vulnerable to the suspended solids in the brines that may obscure the "true" scaling rate.

2. Flowing the brine through screens at the high temperature test point ($\sim 200^{\circ}\text{C}$) was unsatisfactory because the usual particulate level in the brine tended to plug the screens and obscure the accumulation of "true" scale. This particulate level was very sensitive to plant upsets (e.g., sudden variations in pressure or flow), and hence so was the screen test. At 200°C it was generally not a reliable indicator of brine scaling tendency. Better results were obtained with screens at 125°C . At this temperature, ~ 24 h were required for a definitive measurement. However, there was still an occasional lack of repeatability in this technique which could not always be explained in terms of plant operating conditions.

3. Use of the 1-inch-i.d. pipe spools, which were epoxy-potted, sectioned, and polished for microscopic examination, appeared to be a reliable semi-quantitative indicator of brine scaling tendency. At least 60-h exposures were required when these specimens were used. Their 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. Tubing sections ($\frac{1}{2}$ -in and $\frac{3}{4}$ -in) exposed in sidestreams at 200 and 125°C had the same problem (however, see point 5 below).

4. The most reliable and precise specimens for assessing scaling, at the time of the November/December test series, were the pairs of thin, flat coupons. Three materials were used: AISI 1009 mild steel, Teflon TFE, and Hastelloy C-276. The mild steel coupons were mounted on a holder that was held in the flange of the pipe spool. The long dimension of the coupon projected downstream in the 1-inch pipe. The Teflon and Hastelloy specimens were mounted at right angles to the flow on Petrolite-probe, 2-in pipe plugs in a 2-in section of pipe. Because excessive scaling or plant upsets leading to high suspended solids levels sometimes created severe obstructions at the steel coupon holder, subsequent tests were done with the steel coupons mounted on 2-in pipe plugs in the 2-in line with the Petrolite probes.

5. Another modification to the system that was introduced as experience was gained during the year was the addition of a third, delay stage operating from a 125°C sample port. This provided brine at 90°C that had been aged ~10 min since flashing to 125°C. As expected, specimens placed at the output of the delay stage scaled more rapidly than at 125°C and this provided a measure of conditions that might be encountered in atmospheric flash and downstream equipment. Tubing ($\frac{1}{4}$ - and $\frac{1}{2}$ -in o.d.) installed at the output of the delay collected thicknesses of scale that could be measured accurately by sectioning in 12-24 h exposures. Although this technique was not used for any of the proprietary additives tested, it is unlikely, in the light of subsequent work, that the proprietary additives would have had an effect on the 90°C scales, because none functioned as a silica precipitation inhibitor.

6. Scale hardness could not be measured as planned because the amount formed was not thick enough for the penetration test. Longer exposure times would be required to obtain suitable specimens.

Results of Proprietary Additive Tests

Most of the tests of the proprietary additives were carried out during November and December of 1978. During that time eight different formulations from eight different companies were tested. The effects of each of these additives were assessed in 3-day runs, during which the full complement of specimens were in place and the stability of the brine at 90°C was assessed. Experiments were also done during this time to evaluate the more rapid methods for scaling rate measurement that were proposed, i.e., flowing the brine through screens and columns containing small steel balls.

All of the results of the November/December, 1978 test series, with the exception of the chemical analyses of the scale deposits and the results of the examination of the pipe spools, were previously presented in a UCID report.¹

The major characteristics of the effluent brine during that period were as follows:

Chloride concentration:	3.60-4.12 Mol/liter
pH:	5.72-5.96
Density at 25°C:	1.145-1.163 g/cm ³
SiO ₂ concentration:	425-516 mg/kg

The GLEF operated continuously during this test period, except for November 14th, when the brine concentrations dropped to the lower values noted. Wellhead pressures were in the range of 250-315 psia and temperatures were in the range of 209-220°C.

Table 1 lists the values of scaling rate found during two runs with untreated brine. These served as the controls against which the performance of the proprietary additives were measured. It can be seen that, although

Table 1. Scaling rates of untreated brine measured during the November/December test series. (Magmamax No. 1 well).

Scaling rate at 210°C, mil/h				
	Coupon			
	Steel Pipe Spool	Steel	Hastelloy	Teflon
Nov. 11-17 ^a	0.014-0.042	0.02	0.01	0.05
Dec. 12-15 ^b	0.030-0.061	0.08	0.02	0.03

Scaling rate at 125°C, mil/h				
	Coupon			
	Steel Pipe Spool	Steel	Hastelloy	Teflon
Nov. 11-17 ^a	0.16-0.28	0.21	0.10	0.11
Dec. 12-15 ^b	0.085-0.31	0.38	0.06	0.09

^a Exposure time: 113h

^b Exposure time: 65h

the roughness of the scale in the pipe makes its thickness measurement uncertain, there is fairly good agreement between the results of the steel pipe and steel coupon specimens. Also, as has been found to be generally true, the apparent scaling rates found for Hastelloy and Teflon are lower than for steel. We believe this is due to two factors: (a) the combined effects of corrosion and scaling on the steel surface vs. only scaling on Teflon and Hastelloy, and (b) less tenacious adhesion of scale on Teflon and Hastelloy. Longer exposure times and thicker scales tend to reduce the differences of scaling rates among the different surfaces.

Table 2 lists the proprietary additives that were given 3-day tests as antiscalants during the November/December test series. These were selected as a result of an industry-wide solicitation in August of 1978. Table 3 summarizes the results of testing of these additives. For the scaling rates, only the comparison of the rates for mild steel are given here. The data for Teflon and Hastelloy are in general agreement.¹

At 210°C, only the Thermosol APS had a beneficial effect on the scale, but the degree of scale reduction was nearly the same as the experimental uncertainty. As noted, several of the additives increased the deposition of scale, possibly as a result of decomposition of the additive itself. At 125°C, most of the additives appeared to reduce the amount of scale on the coupons, but only two, Drewspers 747 and SC-210, reduced the scale on both the pipe spool and coupons. These two also showed the lowest rates on Teflon and Hastelloy, but they were not lower than the values for untreated brine. Thus the diminished scaling rates shown by Drewspers 747 and SC-210, as well as some of the other additives, as shown in the data of Table 3, may be due only to some action as either a corrosion inhibitor or an agent in preventing the adherence of corrosion product.

An indication of the corrosion rates of mild steel in the brine in the presence of these additives was obtained by measurements using the Petrolite Instruments Company linear-polarization resistance (LPR) equipment. The locations of these LPR probes in the brine streams is shown in Figure 1.

Table 4 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-h of specimen exposure and in all cases these values held nearly steady for the duration 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 lower scaling rate at this temperature (see Table 3) suggests that it may have exhibited some scale inhibition.

Table 2. Proprietary Additives Tested in November - December, 1978 Test Series

<u>Product Name</u>	<u>Company, Address</u>	<u>Chemical Type</u>	<u>Concentration Tested, ppm</u>
Geomate 256	Dearborn Chemical Corp., Lake Zurich, IL	Phosphonate + Polymer	35
CL-165	Calgon Corp., Pittsburgh, PA	Polymer mixture	18
Drewperse 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

Table 3. Performance of eight proprietary additives as antiscalants in Magmax No. 1 brine. (See Table 2 for further details of additives).

Additive	% Reduction of scale on mild steel				90°C silica precipitation test
	210°C		125°C		
	Pipe Spool	Coupon	Pipe Spool	Coupon	
Geomate 256	0	0	0	32	Negative ^b
CL-165	0	0 ^a	0	32	Negative
Drewsperser 747	0	0 ^a	30	50	Negative
Betz 419	0	0	0	52	Negative
Thermosol APS	30	30	0	50	Negative
S-404	0	0	0	21	Negative
SC-210	0	0 ^a	80	42	Negative
Cortron R-16	0	0	0	0	Negative

^a Significant increase in the deposit.

^b No effect on the rate of precipitation of silica.

Table 4. Corrosion rates of mild steel (AISI 1018) in additive-treated brine measured by the linear polarization resistance technique.

	Corrosion rate, mpy	
	210°C	125°C
Control A	9	14
Control B	7	15
Geomate 256	3	15
CL-165	5	2
Drewsperse 747	7	15
Betz 419	7	4
Thermosol APS	7	5
S-404	5	3
SC-210	5	25-60
Cortron R-16	7	25

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. In the case of acidification with HCl, it is not only the pH lowering that is responsible for increased corrosion rates, but also the absence of protective silica scale.

In our "standard" precipitation test,⁹ in which the effluent brine, previously treated with the candidate additive in the plant, is held at 90°C to follow the kinetics of the precipitation of silica, we found that none of the proprietary additives had any effect. This was in contrast to the effect of several generic compounds that had been discovered earlier.²

In the November/December test series, one of these compounds, Natrosol 250LR (Hercules hydroxyethylcellulose) was included with the proprietary additives for evaluation. In-plant injection revealed that it did inhibit the precipitation of silica at 90°C, but it too failed to significantly retard the formation of scales at higher temperatures.

All of the results of this test series, taken as a whole, led us to the conclusion that none of the proprietary additives, except possibly Southwest Specialty Chemical's SC-210, merited further attention as geothermal scale inhibitors.

Precipitation Tests of Additional Proprietary Additives

Work subsequent to the November/December, 1978 test period was devoted mostly to investigations of compounds whose identities were known, i.e., generic compounds. However, the state of the art in water treatment was still advancing, and periodically other proprietary additives and mixtures came to our attention that appeared to be worthwhile evaluating. None of these was subjected to a complete scale-abatement test, but a number were subjected to plant injection and measurement by the precipitation-inhibition test. These additional compounds, together with other pertinent information, are listed in Table 5. None of these compounds showed any activity toward silica at 90°C.

Polysperse Plus was of particular interest because experiments conducted at the GLEF by Paul Henry of the NUS Corporation indicated that it inhibited silica precipitation. It failed in two trials at our facility and, although his experimental approach was somewhat different than ours, we have never determined why these results were in disagreement.

As can be seen from the identities of the proprietary compounds in Tables 2 and 5, most of the materials are the anionic-type polymers traditionally used in various water treatment applications. Although they represent the industry's best guess as to effective antiscalants for hypersaline geothermal brine, in our tests they have certainly not appeared promising. In contrast, as discussed below, cationic polymers have emerged from our generic chemical testing as definite economic possibilities for scale control.

Table 5. Additional proprietary additives tested as silica precipitation inhibitors.

<u>Additive</u>	<u>Company, Address</u>	<u>Chemical type</u>	<u>Concentration tested, ppm</u>
Polysperse Plus	Betz Laboratories Trevose, PA	?	20
Geomate 259	Dearborn Chemical Lake Zurich, IL.	?	40
XFS-43075	Dow Chemical Midland, Mich.	?	40
XD-30469.00	Dow Chemical Midland, Mich.	copolymer of acrylic acid & hydroxyethylacrylate	20
Darex 41s	W.R. Grace Lexington, Mass.	carboxylated polyelectrolyte	20
Visco 3744	Nalco Chemical Houston, Tex.	acrylic polymer + surfactant	20
Belclene 200	Ciba-Geigy Ardsley, N.Y.	low M.W. carboxylic acid	20
Pyronate 40	Witco Chemical New York, N.Y.	low M.W. alkyl aryl sulfonate	20

Experiment With Sludge Seeding to Retard Scale Formation

Another approach to scale control that has been attempted by other investigators for other geothermal brines (see for example, Ref. 11) 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^{12,13} 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 μ m 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 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. The apparent amount of scale accumulated on the mild steel coupons was estimated,¹ but the values are very inaccurate because of the accumulation of sludge and the short duration of the run.

Perhaps a better indicator of the potential of the technique was the lack of scale on the pipe spools. On examination of these specimens, only corrosion product was seen, although the shortness of the run mitigates the conclusions somewhat.

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 6, 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 6) seeding reduced the level of dissolved (particle size $<1\ \mu\text{m}$) 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.

Table 6. Measurements of concentration of "Dissolved Silica" in brine during seeding experiment.
(Concentrations of SiO_2 in mg/kg)

210°C			
<u>Before Sludge Addition</u>	<u>After Sludge Addition</u>		
	<u>0.3 gpm</u>	<u>0.15 gpm</u>	
453	431	416	
125°C			
<u>Before Sludge Addition</u>	<u>After Sludge Addition</u>		
	<u>0.3 gpm</u>	<u>0.15 gpm</u>	<u>0.15 gpm^a</u>
516	306	306	396

^a Immediate acidification of sludge-containing brine

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.

Corrosion rates estimated by the LPR technique during the seeding experiment yielded values of 10 and 14 mpy and 210 and 125°C, respectively, which are not significantly different from the rates found for untreated brine.

From these limited data it appeared 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, and (c) different test surface configurations will have to be devised to measure scaling rates in the presence of sludge.

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

Test of Austral-Erwin Process for Scale Control

The results of the short test of sludge seeding indicated that it would be very difficult to carry out a longer duration test in the LLL facility, without considerable modification, which would be definitive in terms of an accurate evaluation of scale abatement. Another proprietary scale control process, devised by R.W. Erwin of the Austral-Erwin Company, had been proposed to us and had shown promise at the Cerro Prieto and Brawley fields. Thus, because the Austral-Erwin process was technically different from those we had previously tested, and further tests of the seeding technique were not easily implemented, we decided to evaluate the Austral-Erwin process instead.

The Austral-Erwin process involves injecting into the brine a water emulsion of a proprietary mixture of cottonseed oil with small amounts of tall oil and other additives which aid in emulsifying the oils. As carried out in the test of the process at our facility, water was metered at 2 gal/h and the oil-additive mixture at ~0.3 gal/day to form a fine spray at the entrance to the brine (see Figure 1). The resulting concentration of the oil-additive mixture in the brine was 40 ppm.

In theory, the process is said to involve a reaction of the fatty acids in the oils with the calcium of the brine to form a soap. In addition, the surface active compounds thus formed, or present in the emulsion, are supposed to coat the metal of the plant and render it hydrophobic. This surface then would have a tendency to repel colloidal silica, which is hydrophilic in nature, thus retarding its adherence and the formation of scale.

The test of the Austral-Erwin additive was performed from March 9-12, 1979, during which time the GLEF was not operating. The effluent brine characteristics during this period were as follows:

Chloride concentration:	3.52-3.67 Mol/l
pH:	5.83-5.95
Density at 25°C:	1.141-1.149
SiO ₂ concentration:	461-479 mg/kg

Magnamax No. 1 wellhead pressures and temperatures were 254-309 psia and 203-215°C, respectively. As is usual when LLL is the sole user of the well, the brine is less concentrated and scaling rates are lower than when the well is at full flow into the GLEF.

The results of the scaling test are summarized in Table 7. Comparing the results in Table 7 for the untreated brine with those in Table 1, the effect of the lower brine salinity in producing lower scaling rates at 125°C is quite evident.

Except for one feature of its performance, the effect of the Austral-Erwin process in general was not very satisfactory. As can be seen in Table 7, only at 210°C in the pipe spool was the scaling rate lower for the Austral-Erwin treated brine. Also, in the pipe spool exposed at 125°C, there was an indication that the scale formed from the treated brine was considerably less adherent--it had flaked off in many places before the specimen could be carefully examined. On the other hand, where the scale was still adhering to the pipe wall, it was quite thick. Scale formed on the flat coupons more rapidly from the treated brine, and the scale at 125°C obviously incorporated a considerable amount of the additive. It was quite oily to touch, and samples lost 50-75% by weight on ignition prior to x-ray analysis. A similar oily scale was formed on perforated disks exposed at 125°C. The delay stage was also operated during these tests, and it was found that there was no decrease in the amount of scale formed at 90°C from the Austral-Erwin treated brine compared to the controls. The additive also had no effect on the precipitation rate of silica in the 90°C effluent brine.

Thus it appears that the Austral-Erwin process may decrease the adherence of the scale on surfaces such as the pipe spools where there is a high velocity flow without excessive eddies. At points where the flow velocity is lower (e.g., in the 2-in pipe), and where there is turbulent flow such as around our specimen coupons, the accumulation of solids is increased. In this respect it resembles the sludge seeding process.

A difficulty with this additive may be that one of its components such as the cottonseed oil (which is a mixture of palmitic, oleic, and linoleic fatty acids) may adsorb on the silica particles rendering them hydrophobic. They then should have a greater than normal tendency to aggregate and form a precipitate. It is also questionable (but it may not be necessary) that the fatty acids form a salt in this naturally acidic brine. An intermittent treatment scheme was proposed in which the additive would be injected periodically -- just long enough to coat the pipe walls, but not so long as to affect all of the nucleating silica -- but funding limitations precluded testing this idea.

Table 7. Scaling rates of untreated brine and brine treated by the Austral-Erwin process. (Magma-max No. 1 well).

<u>Scaling rates at 210°C, mil/h</u>				
	<u>Steel Pipe Spool</u>	<u>Coupon</u>		
		<u>Steel</u>	<u>Hastelloy</u>	<u>Teflon</u>
Untreated ^a	0.07	0.05	0.02	0.02
Austral-Erwin ^b	0.02	0.08	0.10	0.08

<u>Scaling rates at 125°C, mil/h</u>				
	<u>Steel Pipe Spool</u>	<u>Coupon</u>		
		<u>Steel</u>	<u>Hastelloy</u>	<u>Teflon</u>
Untreated ^a	0.11-0.16	0.10	0.03	0.04
Austral-Erwin ^b	0-0.96 ^c	0.60	0.10	0.12

^aExposure time: 88h

^bExposure time: 65 h

^cSee text

Chemical Analyses of Scales

The scales that were deposited on the coupons were analyzed by x-ray fluorescence and emission spectroscopy to provide additional information on the effects of the brine treatment. Most of the samples that were analyzed were taken from the Teflon coupons so that the effects of substrate corrosion would not be included in the measurements. Scale samples from all three types of coupons were analyzed for the control experiments with untreated brine.

The compositions of the scales are given in Tables 8 and 9. Here it can be seen that even the high temperature scale (formed at 210°C; see Table 8) contains over 50% silica, and the 125°C scales (see Table 9) are 80-95% silica. This lends weight to the contention that control of silica deposition is the key to the control of scale in virtually all portions of a geothermal system downstream of the first steam separation.

Few correlations can be made between the elemental analysis data and the quantities and visual appearances of the scales formed as a result of the brine treatments. One ever-present complication is that the concentrations of the constituents of the brine are not monitored all the time, thus an unusual result for the composition of a scale deposited during these short-term tests may represent merely a transient condition in the brine. At 210°C (see Table 8), the most striking feature of the scales that formed is the high concentrations of copper when additives were present compared to when the brine was untreated. The Cortron R-16 scale also contained large amounts of nickel. This scale and several others had a distinctly greenish tint.

These scales were not analyzed by x-ray diffraction analysis, however, the large amounts of iron, copper, and sulfide suggests that the compounds Cu_2S and CuFeS_2 , previously identified in similar scales,^{14,15} are probably present in these samples. The high sodium, potassium, calcium, and chloride levels, together with the lower silica level in the Drewspere 747 scale show that this scale incorporated some of the brine, and this may be

Table 8. Elemental analyses of scales deposited on Teflon TFE coupons at 210°C from brine treated with various additives (Magmamax No. 1 brine, 4.1 Mol/l chloride)

Element	Controls		Geomate 256	CL-165	Drewperse 747	Betz 419	Thermosol APS	Natco S-404	SC-210	Cortron R-16	Sludge
	7-B	12-A	8-A	8-B	9-A	9-B	10-A	10-B	11-A	11-B	12-B
Si as SiO ₂	60	54	49	60	41	54	51	51	51	30	58
Fe	24	18	23	20	17	19	22	21	21	18	24
Ca	1.4	2.2	1.9	1.7	4.2	1.0	1.0	5.4	1.7	5.2	1.4
Cu	0.3	0.3	3.5	1.2	2.1	4.3	3.6	2.3	4.3	9.2	1.9
Ni	0.01	0.01	0.01	0.7	0.01	1.4	0.01	0.01	0.01	4.8	1.9
Pb	0.3	7.6	0.2	0.05	0.95	0.4	0.1	0.4	0.05	0.8	0.2
Mn	1.6	1.0	1.1	1.4	0.9	0.8	0.9	1.0	0.9	0.7	1.0
Na	0.9	0.3	0.14	0.14	2.5	0.4	0.07	0.56	0.4	1.2	1.5
K	0.1	0.3	0.2	0.1	1.2	0.2	0.05	0.3	0.2	0.1	0.1
Zn	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.1	0.2	0.07
Cl	0.2	0.2	0.2	0.2	5.5	0.2	0.2	0.6	0.2	0.4	0.2
S	0.1	0.9	2.6	0.9	2.2	2.7	3.4	1.3	2.6	5.6	0.2
Al	0.5	0.4	0.5	0.3	0.4	0.5	0.15	0.3	0.4	0.2	0.1
Ag	0.03	0.04									

Ba, Sr, P, B, Rb, Sb,

Cr, Mg, As all <0.1 except 9-A was 5% Mg and 11-B was 0.1% As.

Table 9. Elemental analyses of scales deposited on Teflon TFE coupons
at 125°C from brine treated with various additives
(Magmax No. 1 brine; 4.1 Mol/l chloride)

Element	Controls		Geomate 256	CL-165	Drewperse 747	Betz 419	Thermosol APS	Natco S-404	SC-210	Cortron R-16	Sludge	Natrosol 250LR
	7-B	12-A	8-A	8-B	9-A	9-B	10-A	10-B	11-A	11-B	12-B	7-A
Si as SiO ₂	83	94	88	83	98	90	96	96	94	77	47	60
Fe	1.1	1.5	0.56	1.2	0.7	0.9	1.3	0.45	1.0	6.7	2.0	5.5
Ca	0.45	0.5	0.80	0.56	0.3	1.0	0.3	0.4	0.5	2.5	5.9	0.56
Cu	0.59	1.2	0.04	0.25	<0.02	0.05	0.2	0.01	1.6	<0.02	1.1	0.57
Pb	0.21	0.06	0.02	0.16	0.1	0.1	0.1	0.02	0.1	0.01	0.33	0.33
Mn	0.20	0.2	0.16	0.17	0.2	0.28	0.2	0.15	0.2	1.4	0.41	1.2
Na	0.5	0.4	0.14	0.3	0.3	0.6	0.3	0.2	0.4	0.2	10	0.3
K	0.8	0.4	0.3	0.4	0.2	1.1	0.4	0.3	0.3	0.3	2.0	0.8
Zn	0.13	<0.02	0.08	0.14	0.07	0.12	0.06	0.09	0.3	0.2	0.13	0.21
Cl	0.08	<0.2	1.1	0.4	<0.2	0.6	<0.2	0.1	<0.2	1.4	14	0.4
S	0.3	<0.1	0.0	0.2	<0.1	0.38	<0.1	0.03	0.08	<0.1	0.24	0.3
Al	0.5	1.0	0.18	0.32	0.6	0.24	0.6	0.24	0.55	0.3	0.03	0.5

Ba, Sr, P, B, Rb

Cr, Mg, As all <0.1

the reason for the observed increase in scaling rate compared to the controls. The additive CL-165 caused the greatest increase in scaling rate at 210°C, but there is no clue in the analysis to indicate why this occurred. High calcium levels for some of the scales may be due to precipitation of the sparingly soluble calcium phosphonate, since many of these additives are phosphonates.

Among the scales formed at 125°C (see Table 9), the Cortron R-16 scale is again quite different from the others. This additive was a mixture containing a filming amine that was designed for corrosion inhibition. A plant upset occurred during its testing, to which we attributed the large accumulation of scale that occurred on the 125°C specimens.¹ However, the reverse could be true, i.e., the upset may have occurred because of the high rate of deposition of scale. In any event, the scale was very soft, powdery, easy to remove, and green in appearance. It had higher concentrations of iron, manganese, and chloride than the others.

The Geomate 256 scale was snow white in appearance, as borne out by its low concentrations of the metal sulfides.

The analysis of the scale accumulated on the Teflon coupon during the sludge seeding experiment is also shown in Table 9. The high levels of sodium, potassium, calcium, and chloride show that large amounts of brine were occluded, and the solids probably include much of the sludge itself.

As noted, none of these additives inhibited the precipitation of silica from homogeneous solution. One substance that did was Natrosol 250LR, a Hercules Company hydroxyethylcellulose, and the results of the analysis of its 125°C scale are also shown in Table 9. It appears to be characteristic of such inhibitors that the solids precipitated in their presence contain less silica and more iron than solids formed from untreated brine. The balance of the composition of the solids in such cases has not been established.

Conclusions and Recommendations

1. From the results of the tests of proprietary additives, i.e., the chemical mixtures and the Austral-Erwin process, we conclude that none of these brine treatments have a very beneficial effect on the rates of scaling from the brine of Magmax No. 1 well. Among the chemical additives, Southwest Specialty Chemical's SC-210 shows 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 is in altering the consistency and adherence of the scale.

2. The addition of sludge as a seeding material for accelerating silica precipitation and lowering the levels of silica super-saturation appears to be viable, but the degree of scale abatement brought about by this treatment could not be assessed. If proper equipment can be used to handle the suspended solids levels that exist with this technique, it should be a fairly successful approach to scale control.

3. Although not detailed here, our parallel studies of generic chemical compounds for geothermal scale control have led to a number types of compounds that inhibit the precipitation of silica and scale formation at the lower temperatures.^{3-6,16} Cationic (nitrogen-containing) polymers and surfactants, and compounds containing polyoxyethylene are the most promising.¹⁶ Two of these compounds were found to retard the growth of the 125°C scale by a factor of 2 to 4, and the 90°C scale by a factor of ~10. Combination of silica precipitation inhibitors with mild acidification is also very effective. Acidification remains as the only method found that reduces the scale formed at 210°C.

Acknowledgments

Design, fabrication, and operation of the Scale Control Test System has been the responsibility of the following: E. Kelly of Kelly Welding Services; R. G. Grogan, F. R. McLain, and A. Echeverria of the LLL Mechanical Engineering Department; R. T. Hasbrouck, W. F. Gee, and N. Rector of the LLL Electronics Engineering Department; L. Allen of E.G.&G., Inc.; and P. Gunning, V. Jackson, and crew from Westec Services, Inc.

APPENDIX

Chemical Analyses of Solids Precipitated from Effluent Brine

Several samples of the solids precipitated from the effluent brine were analyzed by x-ray fluorescence techniques to provide a comparison between the chemistries of the two wells, Magmamax No. 1 and Woolsey No. 1, and for comparison with the results of previous test series. Baseline data were obtained for the first time for the rate of precipitation of solids and silica from Woolsey No. 1 brine, and it was expected that the high concentrations of barium and sulfate in this well fluid (150 and 108 mg/kg, respectively, in the effluent brine) would be evident in the results. The kinetic curves are shown in Figure 2 and the results of the analyses of the solids at various times during the incubation are given in Table 10. These measurements were made by means of our standard precipitation test procedure.⁹

At 1 h, the composition of the solids does not differ appreciably from that typically found for the solids precipitated from Magmamax No. 1 brine. However, at later times, there is a pronounced increase in the percentage of barium, calcium, strontium, and sulfur, indicating that the sulfates of these metals are precipitating. This also is probably the reason for the appearance of a second plateau in the suspended solids curve in Figure 2, beginning at ~10 h. This apparent induction period for the precipitation of barium sulfate, especially, has been noted before (Ref. 17, and references therein). Data are also listed in Table 10 for the compositions of the solids obtained as a result of incubations at 70 and 50°C, which were carried out to measure the solubility of silica at these temperatures.⁹ Here it is seen that there is no additional metal sulfate precipitation compared to that at 90°C.

Table 10. Elemental analysis of solids precipitated from untreated Woolsey No. 1 effluent brine as a function of time of incubation (pH = 5.8, 4.13 mol/l chloride).

Element	90°C				70°C	50°C
	1 h	48 h	319 h	535 h	353 h	353 h
Si as SiO ₂	87.9	76.1	63.3	61.3	62.0	64.8
Ba	0.0	5.2	14.5	15.3	14.8	15.7
S	0.1	1.3	3.4	3.6	3.4	3.7
Fe	2.4	2.7	3.1	3.1	2.8	1.4
Ca	0.45	2.2	2.2	2.2	2.5	2.6
Sr	0.007	0.38	0.85	0.59	0.48	0.58
Mn	0.20	0.21	0.25	0.22	0.16	0.12
Zn	0.26	0.20	0.17	0.12	0.12	0.10
K	0.33	0.34	0.24	0.25	0.26	0.35
Na, Al, Mg, P, As, Ni, Cu, Rb Cr, Ag	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

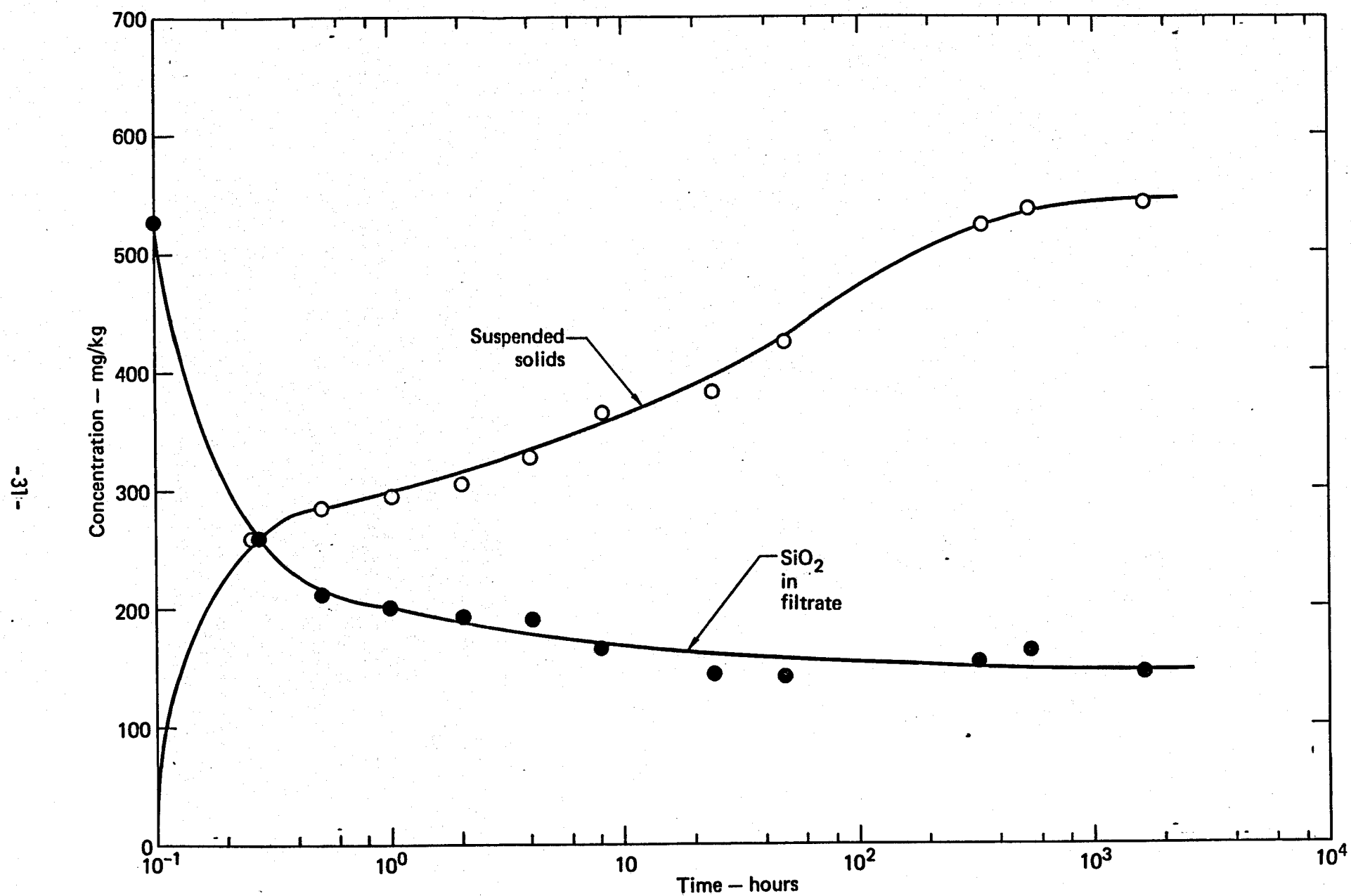


FIG. 2. Concentration of suspended solids and dissolved SiO_2 in effluent brine after incubation at 90°C (Woolsey No. 1 brine, 4.1 mol chloride/liter).

The increased quantity of solids and change in their composition resulting from the precipitation of barium sulfate may only be of academic interest. Unless hold-up times are quite long, it does not appear that it would greatly affect the operation of solids removal equipment such as reactor/clarifiers, and only minor amounts of barium sulfate (0.55% Ba) have been found in the scale deposits formed from effluent Woolsey brine at the Geothermal Loop Experimental Facility of the San Diego Gas & Electric Company.

Dramatic changes in the extent of precipitation and composition of solids as a function of the time of incubation have never been observed for brine from Magmamax No. 1 well. The concentrations of barium, calcium, and strontium in Magmamax brine are virtually the same as those in Woolsey brine, but the sulfate concentration is about a factor of two lower, 41 mg/kg. Evidently this difference is very significant, because the fraction of metal sulfates in solids from Magmamax brine has always been low. An increase in barium sulfate in the solids and scales formed from Magmamax brine is observed, however, when the brine is acidified. This was first noted during experiments with brine acidified to pH 4.5 in the four-stage flash system.¹⁷ More recent measurements, presented in Table 11, show the same effect, but as yet there is no convincing explanation for it.

Table 11. Elemental analyses of solids precipitated from Magmamax No. 1 effluent brine (3.6-4.1 mol/l chloride; incubation at 90°C for times indicated).

<u>Element</u>	<u>Brine acidified to pH 4.0; 120 h</u>	<u>Untreated brine; 197 h</u>
Si as SiO ₂	87.5	91.3
Ba	2.7	0.39
S	0.70	~0.06
Fe	0.38	1.4
Ca	0.49	0.5
Sr	0.21	0.02
Mn	<0.005	0.12
Zn	0.01	0.18
K	0.07	0.30
Na	<0.2	0.9
Cl	<0.02	0.7
<hr/>		
Mg, Al, P, Cr, Ni, Cu, As, Rb, Pb	<0.1	<0.1

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Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.