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ON-LINE TESTS OF ORGANIC ADDITIVES FOR THE INHIBITION OF THE PRECIPITATION OF SILICA FROM HYPERSALINE GEOTHERMAL BRINE

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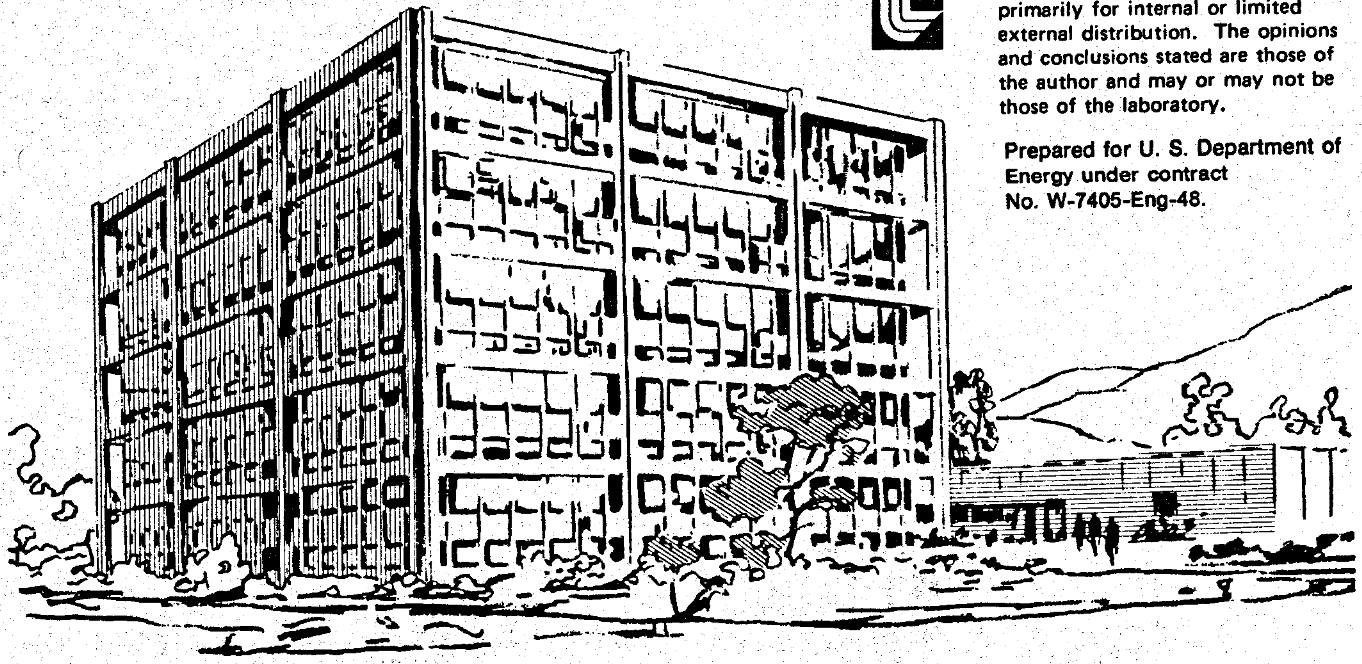

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Abstract

A number of compounds have been screened as potential scale control agents by examining their effect on the precipitation of silica from Magmamax No. 1 brine. The substances were tested using the Lawrence Livermore Laboratory scale-control test system at the Niland, California, test site. Solutions of the test substances were injected into flowing brine at ~200°C, the brine was flashed to 125°C, and then the kinetics of solids and silica precipitation from effluent brine held at 90°C were measured. Compounds tested include a variety of cellulose derivatives, ethylene oxide polymers, several polyethoxylated surfactants, and a phosphonate. The ethylene oxide moiety was confirmed as the source of activity in substances that inhibit the precipitation of silica at 90°C, and the polyethylene glycols in the molecular weight range of approximately 10,000 to 100,000 are the most effective. A brief, in-plant scaling test with the most promising precipitation inhibitor showed that, although it significantly retarded scaling at 90°C, there was no improvement at 125°C or higher, and at 125°C there may have been a slight increase in scaling rate.

Introduction

Since late 1977, in a program aimed at finding an equally effective alternative to the technique of brine acidification for geothermal scale control, the Lawrence Livermore Laboratory has been screening and evaluating a number of commercial organic and inorganic chemicals as inhibitors of silica precipitation and scaling. The first bench-scale tests[1] revealed that many compounds containing the ethylene oxide moiety, $-CH_2-CH_2-O-$, were effective in stabilizing colloidal silica in geothermal brine. In subsequent plant-type tests at the Salton Sea Geothermal Field, in which potential additives were injected into flowing brine at wellhead temperatures,[2,3] one such ethoxylated compound, a hydroxyethylcellulose, emerged as the most powerful inhibitor of silica precipitation at 90°C; however, it failed to retard the formation of geothermal scales at test temperatures of 210°C and 125°C.[3] Also failing to exhibit inhibition of silica precipitation and showing only marginal promise as antiscalants were a series of compounds representing the state of art (Fall, 1978) in commercial proprietary mixtures for scale control in boilers and other geothermal applications.[3]

The principal subject of the present report is an investigation of the activity toward geothermal silica of a variety of substituted cellulose compounds, the class of which only one member had been tested previously, and a series of polyoxyethylene compounds. Several other chemicals of potential promise as antiscalants also have been tested. In this work we hoped to gain further knowledge concerning the specific interactions between collidal silica and the active compounds, and perhaps find a more effective inhibitor than the erstwhile leading candidate.

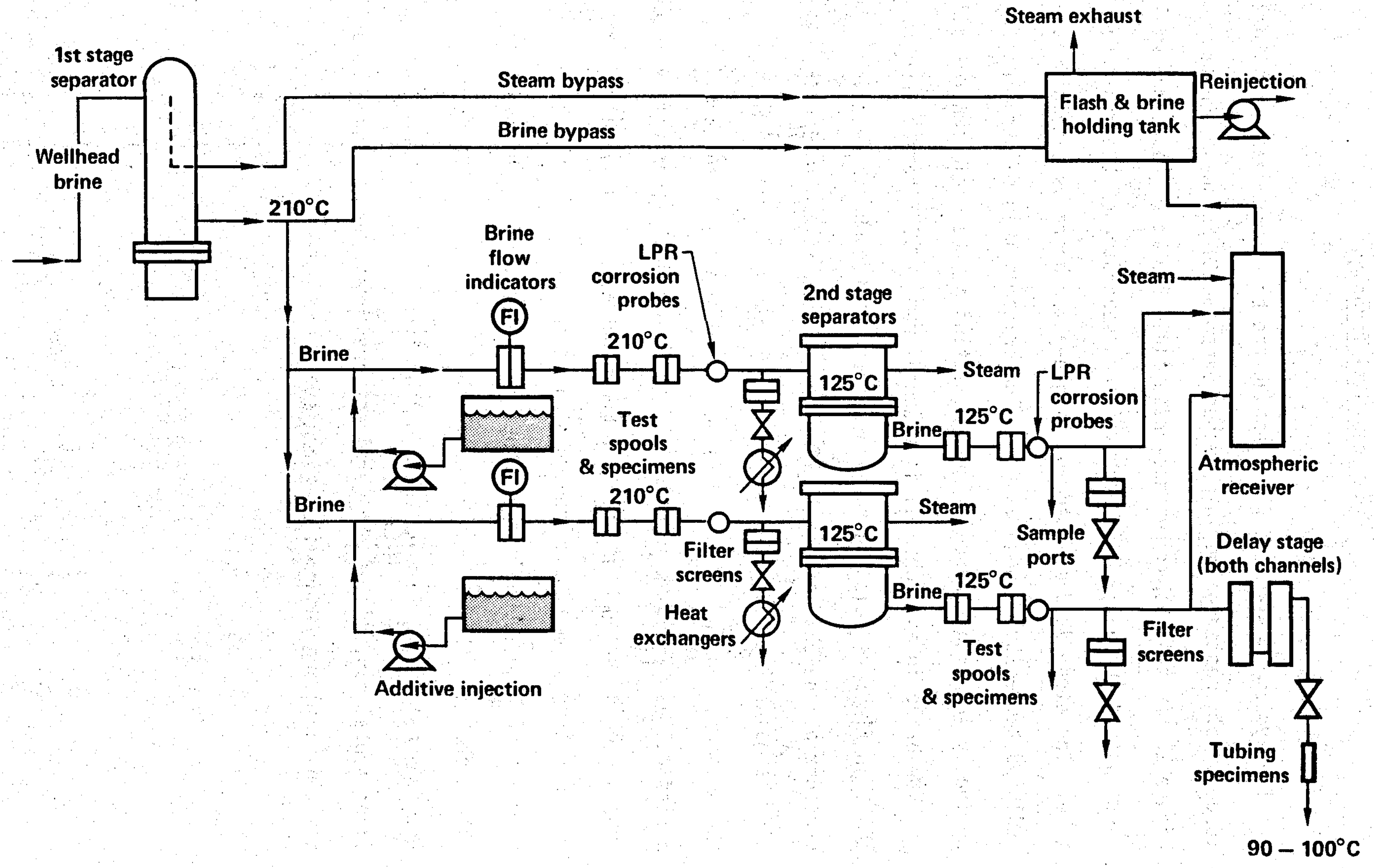
Experimental Technique

The system constructed for flashing the brine and measuring the scaling tendency of treated brine in previous experiments is shown schematically in Figure 1. In this apparatus two-phase fluid from the geothermal well is first passed through a C-E Natco wellhead separator of the centrifugal type. The steam is discarded and single-phase brine is obtained at nearly wellhead temperature and pressure. The brine is then divided into two nominally identical channels for the testing of the scale control additives.

The brine in each channel is flashed from ~200°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 is about 15 psig. Brine flow is 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 is cleaned periodically. Additive solution (at about 0.5-1.0% strength) is metered into the brine using high pressure pumps equipped with pulsation dampeners, and this flow is monitored and maintained in the range of 0.02 to 0.04 gpm by means of Flow Technology turbine flow meters. The additive solution is 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 are monitored and recorded continually.

FIGURE 1

SCALE-CONTROL TEST SYSTEM



The accuracy of the control of additive concentration is determined by the precision of the control of the brine and additive solution flows. This was measured by injecting cesium ion tracer into the brine in the same manner as the additives and then analyzing the brine for cesium using atomic absorption spectrophotometry. It was found that the additive concentrations could be controlled within ± 10% of the nominal values. The additives were metered to provide the nominal concentration at the high-temperature point of addition; this concentration increases ~15% after the second-stage flash because of steam loss.

To test the kinetics of the precipitation of silica in the presence of the various additives, the system was operated from Magmamax No. 1 well. For this well, the separated brine temperature and pressures were 200-220°C and ~260 psia, respectively. Additive solutions were prepared at least 4 hours in advance of use; they were subjected to the ambient outside temperature range of 5-30°C during the period of testing. Several additives required dispersal in a non-solvent such as isopropanol, methanol or acetone before dissolution in water. Starpol 100 was first dissolved in boiling water.

Several control runs without additive injection were carried out during the course of these experiments, but in most cases both channels of the system were used simultaneously for testing additives. Four additives, each at two concentrations, could be tested in a 12-hour period. For each test, additive flow at a given concentration was maintained for 2-hours prior to brine sampling, and then additive flow was terminated with brine flow maintained for 2-hours to flush out the system.

The effect of the additives on the precipitation of silica was measured as reported previously.[1,4] Brine samples were collected for study from the 125°C sampling ports. As collected, the brine flashed to 105°C. It was then placed in air-tight, Viton-gasketed, 130-ml, screw-cap glass bottles and incubated at 90°C. At intervals of 30 min. and 1 hour after sampling, the bottles were opened and the contents filtered through fine-porosity glass crucibles. The silica remaining in the filtrate was measured by atomic absorption spectrophotometry using the method of standard additions. The collected solids were dried in air at 105°C and weighed as a measure of the suspended solids concentration of the brine. Measurement of the silica in this manner has been shown to yield values for the total concentration of silica not retained by the filter (monomeric, polymeric, and particulates $<1\ \mu m$ in size). The initial concentration of silica in the brine sampled at the effluent port was determined in samples immediately acidified with hydrochloric acid.

Additives Tested

A list of the substances tested and their salient characteristics is given in Table 1. The first substance listed, Natrosol 250LR, is the compound that heretofore in our testing has been the most effective inhibitor of silica precipitation. The other hydroxyethyl cellulose (HEC) compounds were selected to provide a range of molecular weights, ionic character, and molar substitution (M.S.). The latter parameter is the average number of moles of ethylene oxide that are attached to each anhydroglucose unit in the cellulose molecule. The low molecular weight HEC compounds comprise about 300 of these units. The CMHEC-420H compound has slightly anionic character and greater high temperature resistance, while the Polymer JR-125 is cationic because of its amine substitution.

The next group of materials in Table 1 are essentially pure ethylene oxide (polyoxyethylene) polymers, selected on the basis of previous testing which suggested that interactions with silica derive from the ethylene oxide moiety.[1] The other cellulose compounds listed have little or no ethylene oxide substitution, but are similar in some of their other properties (e.g., water thickening) to the HEC compounds.

Four additional proprietary antiscalant mixtures were also tested. As reported previously,[3] eight other proprietary mixtures showed no activity toward silica at 90°C in tests similar to those we report here.

The next group of compounds include seven surfactants which were found in our early bench testing[1] with acidified brine to strongly inhibit silica precipitation. The compounds Conco NI-125 and Pluronic F38 were selected late in our testing to provide a comparison with the Carbowaxes.

Table 1. Organic and Inorganic Compounds Tested as Inhibitors of the Precipitation of Silica from Hypersaline Geothermal Brine.

Trade Name	Manufacturer	Mean Molecular Weight	Other Characteristics
Hydroxyethyl Celluloses:			
Natrosol 250LR	Hercules	85,000	M.S. ≈ 2.5, Nonionic
Natrosol 250HR	Hercules	1,000,000	M.S. ≈ 2.5, Nonionic
Cellosize QP-09-L	Union Carbide	85,000	M.S. ≈ 1.8, Nonionic
Natrosol 180LR	Hercules	85,000	M.S. ≈ 1.8, Nonionic
Natrosol 420H	Hercules	1,000,000	M.S. ≈ 4.2, Nonionic
CMHEC-420H	Hercules	85,000	M.S. ≈ 4.2, with carboxymethyl substitution
Polymer JR-125	Union Carbide	100,000 (est.)	Amine-substituted, for cationic character
Ethylene Oxide Polyers:			
Polyox WSRN-80	Union Carbide	200,000	$HO(CH_2CH_2{-}O)_nH$
Polyox WSRN-10	Union Carbide	100,000	"
Carbowax 14,000	Union Carbide	14,000	"
Carbowax 6,000	Union Carbide	6,000	"
Carbowax 1,000	Union Carbide	1,000	"
Carbowax 350	Union Carbide	350	$CH_3O(CH_2CH_2{-}O)_nH$
Other Cellulose Compounds:			
XD-8918.00	Dow Chemical	15,000	Hydroxypropyl Methylcellulose
Tylose MHB	American Hoechst	High	Methyl Hydroxyethyl Cellulose
Marasperse N-3	American Can	?	Modified Sodium Lignosulfonate
Starpol 100	A. E. Staley	?	Acrylamidomethyl-substituted Starch

Table 1. (Cont'd)

Trade Name	Manufacturer	Mean Molecular Weight	Other Characteristics
Proprietary Mixtures:			
Geomate 259	Dearborn	-	Antiscalant for geothermal applications
XFS-43075	Dow Chemical	-	Antiscalant
Polysperse Plus	Betz	-	Antiscalant for geothermal applications
Visco 3744	Nalco	-	Low M.W. acrylate + nonionic surfactant
Other Organic Compounds:			
Ethomeen C/25	Armak	860	Polyoxyethylene(15) cocoamine[a]
Ethomeen 18/60	Armak	2400	Polyoxyethylene(50) octadecylamine
Surfactant AR-150	Hercules	?	Polyoxyethylene glycol ester of rosin
Surfynol 485	Air Products	∿ 1500	Polyoxethylene(30) acetylenic glycol
Tween 20	ICI America	∿ 2000	Polyoxyethylene(20) sorbitan monolaurate
Zonyl FSN	DuPont	?	Fluorinated nonionic surfactant
Zonyl FSB	DuPont	?	Fluorinated amphoteric surfactant
Conco NI-125	Continental Chemical	∿ 9000	Polyoxyethylene(200) nonyl phenol
Pluronic F38	BASF-Wyandotte	∿ 5000	Polyoxyethylene polyoxypropylene copolymer
Dequest 2060	Monsanto	525	Diethylenetriamine pentamethylene phosphonic acid
Inorganic Compounds:			
Potassium Dihydrogen Phosphate		136	KH_2PO_4
Aluminum Chloride		133	$AlCl_3$

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[a] Number in parentheses denotes the number of moles of ethylene oxide per molecule of compound.

Like the Carbowaxes they are medium weight molecules rich in ethylene oxide, but unlike the Carbowaxes they have both a hydrophilic (ethylene oxide) and a hydrophobic (lipophilic) portion, thus have considerable surfactant character. The other surfactants tested (except for the Ethomeen 18/60) contain relatively little ethylene oxide, and the HEC compounds are only weakly surface active.

The phosphonate Dequest 2060, was also tested. It has met with some success in the abatement of calcite-type geothermal scales.[5]

Also tested were two inorganic compounds, potassium dihydrogen phosphate, which previously exhibited activity,[1] and aluminum chloride. Aluminum ion was tested because of its known strong interaction with silca species under certain conditions.[6]

Results and Discussion

To permit detailed intercomparison of the results for different additives, all of the kinetics measurements of the present work were carried out under nearly constant brine chemistry conditions. This was accomplished by scheduling the experiments during the periods when LLL was the sole user of Magmamax No. 1 well: July, 1978, and February-March, 1979. The ranges of brine characteristics during these tests were as follows (effluent brine, flashed to atmospheric pressure):

Chloride Concentration:	3.4 to 3.7 Mol/liter
pH :	5.8 to 6.0
Density at 25°C :	1.135 to 1.145 g/cm^3
SiO_2 Concentration :	450 to 500 mg/kg

During each of the two test periods, the ranges were still more narrow. Control tests with untreated brine also were conducted, and these results serve as a baseline for comparison with the additive tests.

Table 2 summarizes the results of the measurements of the suspended solids and silica in the incubated brines after treatment with the various additives. Only the 1-hour incubation data are presented for brevity; the 30-min. data were always consistent with those at 1-hour. For most of the cellulose compound and ethylene oxide polymer experiments, the general procedure was to test the additive first at a concentration of 40 ppm, then if activity was exhibited, move to the lower concentrations. A concentration of 40 ppm is higher than the economic limit for most additives. We assumed that if no stabilization of the colloidal silica was observed at 40 ppm, there could be no improvement at lower concentrations.

Table 2. Concentrations of Suspended Solids in Brine and Percentage of Silica Retained in Filtrate after Incubation for 1-hour at 90°C. Magmamax No. 1 Brine (3.4-3.7 Mol/l chloride). (Concentration of additive underlined)

Additive	Concentration of Suspended Solids, mg/kg		Silica Retained, %	
Control, no additive:				
Mean value, 5 runs	257 ± 38		47 ± 4	
Hydroxyethyl Celluloses:	40 ppm	20 ppm	40 ppm	20 ppm
Natrosol 250 LR	a	90	86	88
Natrosol 250HR		122		69
Cellosize QP-09-L	163	169	70	69
Natrosol 180LR	158	142	72	74
Natrosol 420H		190		65
CMHEC-420H	170	138	76	68
Polmer JR-125	120	125	85	68
Ethylene Oxide Polymers:	40 ppm	20 ppm	40 ppm	20 ppm
Polyox WSRN-80	244	252	50	50
Polyox WSRN-10	62	73	78	79
Carbowax 14,000	38	31	89	95
Carbowax 6,000		69		84
Carbowax 1,000		179		66
Carbowax 350	200		62	
Other Cellulose Compounds:	40 ppm	20 ppm	40 ppm	20 ppm
XD-8918.00	257	229	49	50
Tylose MHB		214		50
Marasperse N-3	219		50	
Starpol 100		268		46

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[a] Solution not filterable.

Table 2. (Cont'd)

Additive	Concentration of Suspended Solids, mg/kg		Silica Retained, %	
Proprietary Mixtures:	40 ppm	20 ppm	40 ppm	20 ppm
Geomate 259	211		45	
XFS-43075	251		46	
Polysperse Plus		270		48
Visco 3744		275		48
Other Organic Compounds:	18 ppm	5 ppm	18 ppm	5 ppm
Ethomeen C/25	153		78	
Ethomeen 18/60	59		92	
Surfactant AR-150	185		69	
Surfynol 485	232		64	
Tween 20	240		63	
Zonyl FSN	274		56	
Zonyl FSB	219		57	
Conco NI-125	110		73	
Pluronic F38	133		74	
Dequest 2060		142		71
Inorganic Compounds:	40 ppm		40 ppm	
KH_2PO_4	259		54	
$AlCl_3$	207		57	
HCl,[a] pH 5 brine	20		80	
pH 4 brine	2		100	
pH 3 brine	0		100	

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[a] Data from reference 4.

A number of interesting trends are revealed by the data of Table 2. First, there is a clear indication that the ethylene oxide moiety does lend activity to a molecule in interacting with colloidal silica. The greater the "concentration" and molecular weight of ethylene oxide in the molecule, the more effectively it retards the precipitation. This is borne out by the findings that (a) the ethylene oxide polymers, in the optimum molecular weight range, especially the Carbowax 14,000, are the most potent inhibitors; (b) substances with little or no ethylene oxide, such as the other cellulose compounds, have no activity; and (c) increasing the amount of ethylene oxide (increasing M.S. value) in the HEC compounds (cf. Natrosol 250LR vs. 180LR) increases their effectiveness as inhibitors. Comparison of the results for Conco NI-125 and Pluronic F38 with those for Carbowax 6000 (where there are approximately equal amounts of ethylene oxide in the three compounds) indicates that the Carbowax is superior. However, all three compounds have a high hydrophilic/lipophilic balance, thus this may not be a very definitive test of surfactant vs. non-surfactant activity.

Secondly, in compounds that contain ethylene oxide, molecular weight (or size) appears to be critical. In this work, the low molecular weight polyethylene glycol, Carbowax 350, had no effect; in previous work[1] similar glycols had the effect of flocculating agents. As the molecular weight of the Carbowax increases, its inhibitor activity increases. The higher molecular weight Ethomeens are the most effective; however, by the same token Surfynol 485 should have been more potent. Too high a molecular weight, $>\sim 200{,}000$, reduces inhibitor action, as indicated by the diminished activity of the Polyox WSRN-80 in the ethylene oxide polymer series and by the lessened activity of the high molecular weight HEC compounds.

Where the additives were tested at both 20 and 40 ppm concentrations, in most cases there was little difference in activity, but for both Natrosol 250LR and Carbowax 14,000, the two best additives, the lower concentration actually improved their response. Polymer JR-125 approached these two in effectiveness at 40 ppm. For Carbowax 14,000, concentrations of 10 and 5 ppm were also investigated, and these data are given in Table 3. Here it appears that there is very little decrease in activity until the Carbowax concentration is less than 10 ppm.

The phosphonate additive, Dequest 2060, showed an intermediate activity toward silica; it may have an advantage for use in these brines because it is also known to inhibit the precipitation of barium sulfate.

The aluminum chloride showed a slight inhibition, but neither KH_2PO_4 nor any of the proprietary additive mixtures had a significant effect on the precipitation of silica.

In reviewing these data, it must be pointed out that the brine used to perform these experiments does not precipitate silica as rapidly as that obtained at full flow of the Magmamax No. 1 well. At full flow, the dissolved solids (and silica) concentrations are higher and this accelerates the rate of precipitation. This is also true of the Woolsey No. 1 well, which will be discussed below, and probably other wells of the Salton Sea Geothermal Field. Nevertheless, although this Magmamax No. 1 brine was less severe, the intercomparisons among additive effects are believed to be generally valid.

It is interesting to compare the effect of the most potent additive, Carbowax 14,000, with that of acidification of the brine to lower pH values. At the end of Table 2 are listed data obtained in earlier experiments[4] with comparable brine. It is estimated that the addition of 10-20 ppm Carbowax 14,000 would be equivalent to acidification to pH ≈ 4.8.

Table 3. Effect of Concentration of Carbowax 14,000 on the Precipitation of Solids and Silica from Geothermal Brine at 90°C. Magmamax No. 1 Brine (3.4-3.7 Mol/l chloride).

	Concentration of Suspended Solids, mg/kg					Concentration of SiO_2 in Filtrate, mg/kg				
Time	0 ppm	5 ppm	10 ppm	20 ppm	40 ppm	0 ppm	5 ppm	10 ppm	20 ppm	40 ppm
0	0	0	0	0	0	474	469	469	460	475
30 min.	218	78	43	27	28	281	431	431	442	436
1 hr.	252	109	49	31	38	215	412	421	436	423
2 hr.	266		145			215		347		

To test the effectiveness of Carbowax 14,000 as an antiscalant, a brief (21-hour) experiment was carried out with the Scale Control Test Sytem in which the additive was injected at a concentration of 20 ppm and various specimens were exposed to the brines to measure the scaling rates. The system was operated with untreated brine in the second channel. For this test, an additional stage was added to the system (see Figure 1). This stage consisted of a vessel whose input was the 125°C brine and whose output was 90-100°C brine aged ~10 min. with respect to the input. The scaling rate of this brine was several times greater than that of the 125°C brine and it was hoped that this would provide a definitive evaluation of the brine treatment in this short duration test.

To measure the scaling rates of the brine at 125°C, the brine was flowed through a perforated disk contained in a Millipore filter holder,[3] and flat mild steel coupons were placed in the drain from the second-stage separator. Coupons were also placed in the 90°C third stage effluent, and this brine was flowed through sections of 1/2 and 1/4-inch tubing.

For the scaling test, the system was operated with fluid from Woolsey No. 1 well. The well was simultaneously being flowed by the San Diego Gas and Electric Company, and it produced considerably stronger brine than that used for the precipitation tests. Its chloride concentration and density were 4.13 Mol/l and 1.166, respectively, and its silica (SiO_2) concentration was 510 to 523 mg/kg. During the scaling test run, samples of the 125°C effluent brine were collected and analyzed by the standard incubation procedure to determine the effect of the additive in Woolsey brine. These results are given in Table 4. Note that the untreated Woolsey brine precipitates silica much more rapidly than the "weak" Magmamax brine -- primarily because of its higher salinity, but also because of its higher

Table 4. Effect of Carbowax 14,000 on the Precipitation of Solids and Silica from Geothermal Brine at 90°C. Woolsey No. 1 Brine (4.1 Mol/l chloride). 20 ppm Carbowax.

	Concentration of Suspended Solids, mg/kg		Concentration of Silica, mg/kg	
Time	Untreated Brine	Treated Brine	Untreated Brine	Treated Brine
0	0	0	526	513
15 min.	258	37	262	467
30 min.	285	70	211	414
1 hr.	296	87	201	328
2 hr.	305		192	
4 hr.	327		192	
8 hr.	363		163	
24 hr.	380		147	

initial degree of supersaturation. At 30 min., 60% of the original silica precipitates from Woolsey brine compared to about 40% from Magmamax brine. The Carbowax is less effective as an inhibitor in Woolsey brine than in the Magmamax brine -- 64% silica retained vs. 95% for the 1 hour incubation -- but it still does significantly retard the precipitation.

In this scaling experiment the apparent corrosion rates of AISI 1018 mild steel also were measured for both the treated and untreated brine using the Petrolite Instruments Company linear polarization resistance (LPR) equipment. Probes were located in both the high temperaure (188°C for Woolsey brine) and low temperature (125°C) lines (see Figure 1). Observed steady-state corrosion rates (in mils per year) were as follows:

	Temperature	
	188°C	125°C
Untreated brine	2	10
Treated brine	3	5

As was found previously in the proprietary additive tests,[3] the observed corrosion rates were higher at the lower temperature, probably reflecting the differing nature of the protective surface films.

In the scaling rate measurements it was found that there was a significant (factor of 2-3) reduction in the scale accumulated on the 1/4-inch tubing exposed to the 90°C effluent brine, as a result of the addition of 20 ppm of the Carbowax 14,000. There was also a corresponding dramatic reduction of scale in the control valve connected to this tubing. However, at 125°C, both the steel coupons and the perforated disk showed increased amounts of scale compared to the amounts on the specimens in the untreated brine. The reproducibility of this measurement is not accurately known, but in any case it is certain that there was no beneficial effect at 125°C. It must therefore be concluded that this additive was, at best, ineffective at this temperature.

The reduction of the accumulation of scale from the "aged," 90°C brine confirms that there is a correspondence between actual scaling behavior and precipitation tests performed at the same temperature. The failure of the additive at 125°C, on the other hand, illustrates the risk in extrapolating the lower temperature results. In our previous work[1-3] the precipitation tests at 90°C pointed up Natrosol 250LR as a promising scale control additive, but it too failed to retard scaling at higher temperatures.[3]

Many of the compounds that we have tested have been used in other applications as protecting agents to stabilize colloidal systems (although not for silica). In those applications, stabilization is usually attributed to the adsorption of the polymers in the form of loops on the surfaces of the precipitating particles, thus sterically preventing the particles from coming sufficiently close for the London-van der Waals attractive forces to lead to flocculation.[7] Our observation that concentrations of additive higher than 20 ppm leads to little improvement in the stabilization of the silica suggests that the particles are "completely" covered at this concentration.

The failure of the additives tested to reduce the scaling at higher temperatures probably is a result of their diminished water solubility as the temperature is increased. The polyoxyethylene and cellulose derivatives characteristically have an inverse solubility/temperature behavior [8,9]; their precipitation from solution takes place at a temperature known as the cloud point. The cloud point of solutions of these substances is also lowered by increasing amounts of dissolved inorganic salts such as those found in the geothermal brines.[8,9] Little work has been done in determining cloud points above 100°C, but it appears from data on a variety of nonionic surfactants[7-9] and unpublished material[10] that the cloud points of the additives which we tested are in the range of 50 to somewhat greater than 100°C. Thus at the 125°C temperature, where much of our scaling rate measurements are made, there may not be enough of the additive in true solution to react with the colloidal silica. In the case of Natrosol 250LR, this may be the reason why very little scale abatement was observed. In the case of the Carbowax 14,000 and the Ethomeens, where there also was apparently an increase in scaling rate at 125°C, the reduced solubility could have led to bridging of the polymers between particles and an enchancement of flocculation. Another possibility is that the precipitation of the additive itself could form a pseudo-scale or provide additional nuclei for precipitation of the silica. Further investigation of these ideas is in progress.

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201-225	9.25	526-550	15.50
226-250	9.50	551-575	16.25
251-275	10.75	576-600	16.50
276-300	11.00	601-up	—[1]
301-325	11.75		

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[1] Add $2.50 for each additional 100 page increment from 601 pages up.

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