

CONF-780708-17

Lawrence Livermore Laboratory

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Geothermal Brine

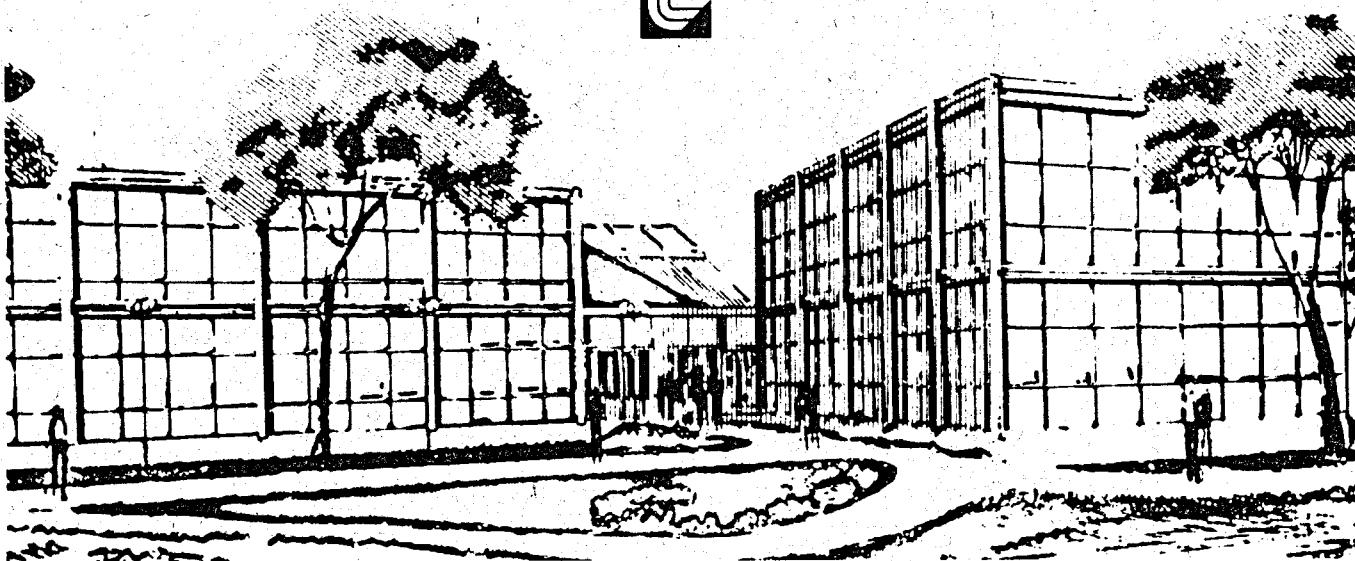
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March 1978

MASTER

This paper was prepared for submission to the Geothermal Resources Council
Meeting, Hilo, Hawaii, July 25, 1978.

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EFFECTS OF ORGANIC ADDITIVES ON THE FORMATION OF SOLIDS FROM HYPERSALINE GEOTHERMAL BRINE*

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INTRODUCTION

An important technical obstacle to the effective utilization of the high-salinity brines of the Salton Sea geothermal field is the rapid precipitation of solids from the brine when it is cooled. These solids are composed primarily of silica with some iron oxides and lesser amounts of heavy metal sulfides--the composition depending on the temperature at which the brine is flashed. Acidification of the brine from a natural pH of ~6.0 to ~4.0 has been shown to significantly delay precipitation and scaling of brine handling surfaces^{1,2}; however, this has the disadvantage of increasing corrosion rates.

Even if acidification is used to control scaling, there still remains the problem of the neutralization of the acidified brine effluent by calcium carbonate in the injection reservoir into which the spent brine is pumped. Return of the pH of the brine to a value of 6.0 enhances the precipitation of the silica and may cause plugging of the pores of the injection well. Thus we have been seeking a brine treatment method that will inhibit the formation of solids (primarily silica), not only in a processing plant, but also when the brine comes in contact with the geologic formation of the injection well.

An approach now being tested is to stabilize the colloidal solids by means of organic compounds such as polymers and surfactants. Use of such materials has previously been considered primarily for solids removal from spent fluids,³ and control of alkaline earth scales,⁴⁻⁶ but no systematic studies of precipitation inhibition for geothermal brines, where silica is the predominant species, have been reported.

The review publications of Iler^{7,8} on the colloidal chemistry of silica are excellent starting points for choosing the types of compounds that might be effective in inhibiting the precipitation of silica from geothermal brine. Most of the emphasis in the literature is on deliberate flocculation of the colloid, rather than stabilization; however, it is known^{9,10} that many compounds that interact with colloidal particles at low surface

coverages to produce flocculation may act as steric stabilizers at higher concentrations and higher surface coverages. Thus a variety of substances were tested, including both simple and polymeric alcohols, ethers, aldehydes, carboxylic acids, amines, amides, cellulose derivatives, and classes of materials such as detergents, surfactants, and coupling agents. An inorganic phosphate, KH_2PO_4 , and a chelating agent EDTA, also were tested.

The ultimate goal of the Lawrence Livermore Laboratory (LLL) brine treatment study is to identify compounds that will, at cost-effective concentrations, inhibit scale and solids formation when added to the brine at the high-temperature (~200°C) front end of the plant. The study reported here constitutes a preliminary, bench-test screening of 49 substances, the most promising of which will be examined later in on-line pilot plant studies. In the present work the additives were mixed with hypersaline brine that had been acidified to pH 4.0 ± 0.3 and flashed to 1 atm, ~100°C, in the LLL Geothermal Field Test Apparatus near Niland, California. The rate of disappearance of dissolved silica from the treated brine was compared with the rate for untreated brine as a measure of the effectiveness of the additive. (Untreated brine is defined here as brine to which only hydrochloric acid had been added.)

EXPERIMENTAL METHODS

The LLL Four-Stage Brine Flash System was operated from Magmamax No. 1 well, and the effluent brine from the final stage was used for the additive experiments. Variations in the flow rate of the well cause the composition of the brine to change by ~25%; in the present work the brine had the following average characteristics: 4.2 M chloride, 22% total dissolved solids, 530 mg/kg (ppm by wt.) SiO_2 , and 233 mg/kg iron.

To test the effect of an additive on the rate of precipitation of solids, samples of the system effluent brine at a temperature of ~100°C were mixed with the test substance, usually to achieve a final concentration of 50 ppm in the brine, immediately sealed under high-purity nitrogen in

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under contract number W-7405-ENG-48.

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special glass ampoules,* and then incubated at 90 ± 5°C for a period of time selected to differentiate the treated brine from the untreated brine. For the pH 4.0 brine this time was 18 to 48 hours. The brine samples were held at 90°C because this is the minimum temperature that spent brines are expected to reach in injection facilities. For the experiments on contacting the brine with CaCO₃, a few minutes were allowed for reaction of the additive with the brine in the open ampoule; then 1 g of powdered, reagent-grade CaCO₃ was added to the brine and the ampoule sealed. This immediately raises the pH of the brine to 5.8.

At the appropriate time of incubation, the ampoules were opened and the contents filtered by vacuum through Kimble No. 28260 or Corning No. 32960 fine-porosity porous-glass crucibles. The solids were collected in the crucible, washed thoroughly with water, and dried in an oven at 105°C. The filtrate was immediately acidified, and then its silica concentration was determined by the method of standard addition using the technique of atomic absorption spectrophotometry.¹¹ The crucibles have a nominal maximum pore size of 4.5-5.5 µm; however, concomitant experiments established that, with a filter cake, the crucibles remove most particles larger than 1 µm in size. It has also been found that the atomic absorption technique quantitatively measures both the truly-dissolved, monomeric silica, and silica in particles at least as large as 5 µm in size.

RESULTS AND DISCUSSION

As is well known,¹ amorphous silica precipitates very rapidly from the hypersaline brines of the Salton Sea Geothermal Field. The concentration of silica in this brine when flashed to atmospheric pressure is over 500 mg/kg, and its equilibrium solubility is ~150 mg/kg. Precipitation at the natural pH of 5.7-6.0 and at 90°C is virtually complete within one hour.¹¹ Acidification of the brine to pH 4.0 extends this time to about 24 hours; however, most of the silica is then in particles in the size range of about 1-50 µm, and because aggregation has not occurred, the solution is difficult to filter. This condition obtains for several days, until flocculation finally takes place.

A total of 49 prospective additives were tested. A few were immediately rejected because they were not sufficiently soluble in room temperature water to make a solution of practical concentration for plant injection. Several additive solutions also caused immediate precipitation upon addition to the hot brine. Many of the additives tested were found to influence not only the rate of growth of the solid particles, but also the filterability of the brine/precipitate mixture. Several agents were found to enhance the rate of precipitation and filterability, and are thus regarded as potentially useful flocculants. These substances, listed in Table 1, produced a very good floc and a solution containing a lower concentra-

tion of silica than the untreated brine for the same incubation time. Such compounds could be useful in mineral recovery operations involving acidified brine effluents, which, as noted, produce filterable solids very slowly, especially at ambient temperatures.

Table 1. Flocculants for silica in acidified (pH 4.0) hypersaline geothermal brine. (24-48 h test)

Compound Trade Name	Manufacturer	Chemical Name
A-1100	Union Carbide	γ-aminopropyl-triethoxysilane
Z-6070	Union Carbide	Methyltrimethoxy-silane
CYAF-5103	American Cyanamid	Proprietary--organic polyelectrolyte
P-400	Dow Chemical	Polyoxypropylene glycol
E-400	Dow Chemical	Polyoxyethylene glycol
	Union Carbide	Mixed polyethylene imines

Among the additives that had the effect of decreasing the rate of precipitation of silica, the ones selected for further testing were those that maintained, for at least 24 hours in pH 4 brine, a level of silica in solution at least 1.5 times higher than that reached in the untreated brine. Table 2 lists these together with the results of the final bench tests. Not included in this group are three marginal substances--resorcinol; Surfynol 465 made by Air Products, which is a polyethoxylated ether of 2,4,7,9-tetramethyl-5-decyne-4,7-diol; and Fluorad FC430, made by 3M, which is a fluorinated alkyl ester. These were intermediate in strength as colloid stabilizers.

The two numbers in each data pair of Table 2 are, respectively, the concentrations of silicon (as SiO₂) remaining in the solution (filtrate) in the presence and absence of the additive, after the specified incubation time. Not only did the group of substances listed in Table 2 effectively inhibit the growth of the colloidal silica, but they, like the flocculants, also produced an easily filtered mixture. In this case, however, the measured solids concentrations were low: 50 mg/kg or less vs. >350 mg/kg for the flocculants, and vs. 550 mg/kg when final equilibrium is established.

In the first test, 28-30 h at pH 4, the Triton X-100 and KH₂PO₄ were definitely inferior, although the latter was quite effective at 150 ppm. The six best additives from the first test were then subjected to an additional test in which CaCO₃ was mixed with the brine after reaction with the additive. This was a very severe test, since very little time was allowed for the additive-silica reaction, and the powdered CaCO₃ provides a large surface area for nucleation of the silica particles. Nevertheless, four of the substances still clearly inhibited silica precipitation, and one, the Ethomeen C/25 stands out in this respect.

*~200 cm³ capacity, designed by J. H. Hill, Lawrence Livermore Laboratory.

Table 2. Additives most effective in inhibiting precipitation of silica from hypersaline geothermal brine at 90°C. (Initial SiO₂ = 530 mg/kg; 50 ppm additives except as noted)

Additive	Manufacturer	Chemical Name	Silica concentration, mg/kg, with additive/without additive		
			pH 4.0 28-30 h	Initial pH= 4.0, then 4 h with CaCO ₃	Bulk price, \$ per 100 lb. ^c
Triton X-100	Rohm & Haas	Phenoxypropoxyethanol	374/237		39
Natrosol 250LR	Hercules	Hydroxyethyl cellulose	462/237	275/183	155
Zonyl FSN	DuPont	Perfluorinated alkyl sulfactant	360/237 ^a		1300
Goodrite K732	Goodrich	Polyacrylic acid	433/313	185/185	95
Glyoxal	J. T. Baker	Ethanedral	495/313 ^a	207/183	500
KH ₂ PO ₄	J. T. Baker	Potassium dihydrogen phosphate	323/313 ^b		41
Vinsol AR-150	Hercules	Polyethylene glycol ester of pale wood rosin	507/208	286/185	56
Tween-20	ICI-US	Polyethoxylated ester of sorbitol monolaurate	489/208	262/183	76
Ethomeen C/25	Akzona	Polyoxyethyl coco-amine	485/208	342/185	70

^a20-25 ppm additive^b75 ppm additive^cQuoted February, 1978

The experiments conducted thus far in this study still do not present a very clear picture of the types of organic moieties and molecules that are most effective in inhibiting precipitation. However, we do have good evidence that among the surfactant-type materials, the nonionic ones are best. This point was specifically examined by testing the series of DuPont Zonyls, which are structurally-similar, fluorinated surfactants differing in their ionic state. Brine at pH 4.3 containing 500 mg/kg SiO₂ was used, and after 140 h at 90°C, the following values were obtained for the silica remaining in solution: nonionic, 445; amphoteric (isoelectric point 4.5, thus slightly cationic here), 397; cationic, 322; anionic, 265; and no surfactant, 170. Thus the degree of interaction of the Zonyls is in the order listed; the observed trend could be related to the fact that the colloidal silica in this solution has a weak negative charge.^{7,8} The nonionic Zonyl was tested further and is the Zonyl FSN listed in Table 2.

Because ethylene oxide (-C-O-C-) blocks are found in five of the final group of additives (Table 2), it is clear that this moiety is an important source of activity, probably because of hydrogen bonding with the silanol (Si-OH) groups of the silica particles. In addition, it is known that chains of ethylene oxide tend to become less soluble at higher temperatures, thus enhancing their anchor capability. The large and polymeric molecules have the advantage of multiple adsorption sites, and they can produce thicker barriers to the aggregation of the silica particles. In most of the colloid stabilizers, in contrast to the flocculating agents, the other part of the molecule is relatively non-polar and hydrophobic. In the case of the Natrosol

250LR, there may be internal hydrogen bonding among the cellulose rings to create a nonpolar exterior. The activity of the glyoxal may be due to the formation of acetal or hemiacetal, giving polymeric structures vaguely related to the successful hydroxyethyl cellulose. The action of KH₂PO₄ may be similar to that of the phosphonate threshold inhibitors,⁴⁻⁶ a class of substances not yet tested in our work.

In hypersaline brine, several unusual circumstances exist. The high concentrations and variety of salts lower the activity of water and mitigate electrostatic repulsion effects. Temperatures are high, and little is known about interactions here. The relative affinity of the functional group for silanol vs. water is of prime importance. The effect of other precipitating solids such as the iron hydroxides is not known. A complex, subtle, and delicate balance of interactions is taking place, and more work is needed before a firm picture emerges.

Because the time available for the field tests was limited, we concentrated our initial efforts mainly on screening as many different substances as possible, without also carefully examining the effect of the concentration of the additives. Nevertheless, this variable is of prime importance, not only for its influence on the chemistry involved, but also because the ultimate usefulness of the additives will depend on their cost. A test of the effect of concentration of one additive, the Natrosol 250LR, was carried out and the results are given in Table 3. As shown here, 10 ppm Natrosol 250LR is near its maximum effectiveness for short-term stabilization.

Table 3. Effect of concentration of Natrosol 25QLR on the precipitation of silica from hypersaline geothermal brine at 90°C. (pH 3.8; Initial SiO₂ = 517 mg/kg)

Natrosol ppm	SiO ₂ remaining in solution, mg/kg	
	41 h	7 days
0	225	188
10	457	196
50	497	311
100	494	329

If a substance such as the Ethomeen were equally effective, we estimate that its use as a brine treatment in a geothermal power plant would cost less than 0.7 mil/kWh, or about 4% of the value of the electricity generated. The organic additives thus show considerable promise as alternatives, or perhaps supplements, to acidification for scale and solids control. The substances found to be best by the bench-scale tests will be evaluated further as scale control agents under actual plant operating conditions, by injection into unacidified brine at high temperature.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

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