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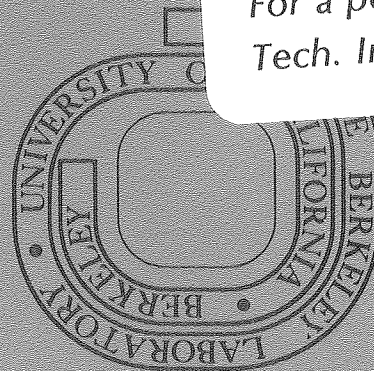
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ABSTRACT

We have studied the precipitation of amorphous silica from synthetic geothermal brines that resemble the flashed brine at Cerro Prieto. We found that part of the dissolved silica quickly polymerizes to form suspended colloidal silica. The colloidal silica flocculates and settles slowly at unmodified brine pH values near 7.35. Raising the pH of the brine to about 7.8 by adding base and stirring for a few minutes causes rapid and complete flocculation and settling. These results have been confirmed in the field using actual Cerro Prieto brine. Several commercially available flocculating agents were also tested. Both in the laboratory and in the field, we found quaternary amines to be effective with some brine compositions but not with others. Polyacrylamides do not work at all.

These results suggest the following simple preinjection brine treatment process: age the brine for 10 to 20 minutes in a covered holding tank, add 20 to 30 ppm lime (CaO), stir for 5 minutes, and separate the flocculated silica from the brine using a conventional clarifier. The brine coming out of such a process will be almost completely free of suspended solids.

The pilot plant tests needed to reduce this conceptual process to practice are discussed.

In a separate study, we researched the rate of deposition of silica scale from synthetic brines. We found that a modest decrease in pH could significantly reduce the scaling rate at a reasonable cost.

INTRODUCTION

The work reported here was conducted in support of the ongoing studies on brine reinjection at Cerro Prieto being conducted by the personnel of the Comisión Federal de Electricidad (CFE) and the Instituto de Investigaciones Electricas (IIE). The work, which was conducted at the Lawrence Berkeley Laboratory (LBL), is part of the CFE-DOE Cooperative Program at Cerro Prieto.

For the purposes of this study, we assumed that the brine to be reinjected would be flashed and separated from steam twice, and that it would be delivered to the brine treatment facility at atmospheric pressure and a temperature near 100°C. These assumptions are consistent with CFE's long-term field development plan. Under these conditions Cerro Prieto brine is supersaturated relative to amorphous silica by about threefold, and the excess silica in solution is rapidly converted to

suspended colloidal silica by homogeneous nucleation and growth of colloidal particles. The flocculation of this colloidal silica and its adhesion to solid surfaces creates the massive white amorphous silica deposits that form throughout the existing surface brine disposal system at Cerro Prieto.

Injecting brine that contains 400 to 500 mg·l⁻¹ suspended solids into a reservoir having pore-dominated permeability, like that at Cerro Prieto, will cause severe formation damage. Therefore, this colloidal silica must somehow be removed prior to reinjection.

The major task assigned to us was to research methods to remove silica from flashed brine to make it fit for reinjection. A secondary task was to study the rate of silica scale deposition from flashed brine at about 100°C and to find a means of controlling it.

The experimental techniques we employed in this work are an extension of the techniques developed during an earlier study of the chemical kinetics of silica polymerization in geothermal-brine-like solutions (Weres et al., 1980b).

The staff of the IIE and CFE laboratories at Cerro Prieto have recently performed similar experiments and confirmed our results (Hurtado et al., 1979). They are presently testing the brine treatment process that we recommended to them on a pilot plant scale, and the results of this work should be available shortly.

The carbonates and sulfates of calcium, strontium, and barium are the materials other than silica most likely to precipitate and cause formation damage after reinjection. This possibility was studied theoretically. The results of this work are reported elsewhere (Iglesias and Weres, 1980).

The contents of this paper and that by Iglesias and Weres (1980) are included in the report by Weres et al. (1980a) which also describes some additional work not discussed here.

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REAL BRINES AND SYNTHETIC BRINES

We studied the precipitation of amorphous silica from Cerro Prieto brines by preparing

synthetic brines that closely resemble them in our laboratory. The approximate chemical compositions of two such synthetic brines, which were extensively used in the silica removal studies, are presented in Table 1. The silica concentrations and pH values shown in the table were those we used most often. However, some work was also done at different silica concentrations and pHs. The concentrations of all other components were always approximately as shown in the table. (The concentration of sodium varied slightly with the silica concentration and pH. Also, evaporation tended to concentrate the brines slightly during the experiments.)

These synthetic brines were formulated to have concentrations of their major components in the same range as real Cerro Prieto brines that have been flashed down to atmospheric pressure. The "high-Ca" formulation was more or less arbitrarily chosen to resemble a "typical" flashed brine at Cerro Prieto.

The "low-Ca" formulation approximately corresponds to a mixture of the waste brine streams from Cerro Prieto wells M-8, M-27, M-31, M-35, and M-46. This composition was chosen because the waste brine line shared by these wells is the source of brine used for most pilot plant work at Cerro Prieto. Chemical components that we consider unlikely to directly affect the chemical behavior of the silica in the brine under the conditions of greatest interest were left out of our synthetic brines.

The pH value 7.3, which we chose for the synthetic brines, is typical of the pH values of freshly flashed brine specimens determined in the field with still-hot brine. These range between about 7.0 and 7.6, and are most often about 7.3 or 7.4 (private communication from A. Mañon M. and our own field measurements).

Also shown are typical analyses of flashed brine from wells M-14 and M-30. We used brine from these wells in our limited field work with freshly flashed brines at Cerro Prieto.

The brines at Cerro Prieto are weakly buffered. The major buffer at temperatures near 100°C and pH values between about 7.2 and 9.5 is monosilicic acid, $\text{Si}(\text{OH})_4$. (Henceforth, "monosilicic acid" will be abbreviated as MSA.) At lower pH values the carbon dioxide-bicarbonate buffer system is dominant. The nature of our experiments was such that it would have been very hard for us to adjust and control the pH of our synthetic brines by relying on these buffer systems alone. Therefore, we included a small amount of the buffering compound barbital (5,5'-diethylbarbituric acid) in our synthetic brine formulation. The pK_a of barbital is about 7.4. Bicarbonate was usually left out of the synthetic brines despite being a relatively important real brine component because it has no direct effect upon the behavior of silica and its presence would have complicated pH adjustment. Boric acid was included because we know that it can have a mild inhibiting effect upon silica polymerization under some conditions (see Veres et al., 1980b, Section 3.15).

TABLE 1. NATURAL AND SYNTHETIC CERRO PRIETO BRINES

	Natural brines*				Synthetic brines			
	Well 14		Well 30		High Ca		Low Ca	
	$\text{mg}\cdot\text{l}^{-1}$	$\text{mmole}\cdot\text{l}^{-1}$	$\text{mg}\cdot\text{l}^{-1}$	$\text{mmole}\cdot\text{l}^{-1}$	$\text{mg}\cdot\text{l}^{-1}$	$\text{mmole}\cdot\text{l}^{-1}$	$\text{mg}\cdot\text{l}^{-1}$	$\text{mmole}\cdot\text{l}^{-1}$
Na	7079	308	7809	340	6970	333	6610	288
K	1439	37	1833	47	1502	38	1436	37
Ca	445	11	596	15	501	12	329	8
Cl	13113	370	15173	428	12940	365	12089	341
SiO_2	960	16	1077	18	1000	17	1094	18
B	18	1.7	17.5	1.6	11	1.0	13.1	1.2
F	2.4	0.13	1.3	0.07				
Sulfate	11	0.11	13	0.14				
Carbonate + Bicarbonate	50	0.82	35	0.57				
As	1.5	0.02	0.47	0.006				
Ba	10.7	0.078	8.0	0.058				
Cu	<0.05	<0.001	1	0.02				
Fe	0.8	0.014	0.5	0.009				
Mn	0.2	0.004	2.6	0.047				
Sr	17.6	0.20	18.8	0.21				
Zn	0.01	0.0002	0.01	0.0002				
Barbital buffer						20		20
pH						7.2-7.4		7.2-7.4
T						95°C		95°C

*Values quoted and recalculated from Cosner and Apps (1978), Records 68 and 106. This data was generated by the CFE Laboratory at Cerro Prieto and kindly provided to LBL by A. Mañon M.

In all experiments, the artificial brine was constituted and silica polymerization initiated by mixing together two preheated solutions, one acid and one alkaline. During the experiments, the "brine" temperature was always between about 92 and 97°C.

SILICA REMOVAL STUDIES: EXPERIMENTAL METHODS

In these experiments the alkaline solution consisted of a premeasured amount of dilute sodium metasilicate solution. The acid solution contained the appropriate amounts of the major component salts, sodium barbital, acid to adjust the buffer pH and neutralize the silica, and water to make up the total desired volume. A total volume of 300 ml was usually employed.

Throughout our work with simulated brines, all volumes were measured at room temperature. Therefore, when we say 300 ml, we mean that the volume would be that if the solution were cooled down to room temperature. When applied to salt concentrations and initial silica concentrations, units of moles or grams per liter are also used in this sense. Because of the relatively low salt content of these solutions and the semi-quantitative nature of most of the synthetic brine data, this is, for all practical purposes, the same as moles or grams per kilogram of water.

The sodium metasilicate stock solution contained about $2 \text{ g}\cdot\text{l}^{-1} \text{ SiO}_2$. Because it was hard to make up this solution to an exact predetermined concentration, it was always standardized by comparison with a standard silica solution (Fischer AA standard).

The desired amount of sodium metasilicate solution was put into a plastic bottle, some of the remaining air squeezed out, and the cap closed tightly. It was then put into a boiling water bath to preheat. (This procedure ensured that the bottle would neither rupture nor lose water when heated.) A separate 50-ml aliquot of the sodium metasilicate solution was titrated with 0.5 M HCl using a pH meter to determine the volume of HCl solution needed to neutralize the given amount of sodium metasilicate solution.

The acid starting solution was prepared from a stock solution of "concentrated brine," a stock solution of sodium barbital, 0.5 M HCl, and water. The concentrated brine was a mixture of sodium, potassium, and calcium chlorides and boric acid in water formulated so that putting 3 parts of it into 20 parts of the final synthetic brine would give the desired final major component concentrations. For example, in the case of the high Ca synthetic brine presented in Table 1, the concentrated brine contained 1.667 M NaCl, 0.256 M KCl, 0.0833 M CaCl₂, and 0.0066 M H₃BO₃. The concentrations of the last three components in this concentrate are simply 20/3 times their desired concentrations in the synthetic brine. The concentration of NaCl is somewhat smaller because the sodium metasilicate and buffer stock solutions also contain sodium.

In the case of the "Low Ca" synthetic brine,

the "concentrated brine" contained 1.547 M NaCl, 0.245 M KCl, 0.0547 M CaCl₂, and 0.0081 M H₃BO₃.

The barbital buffer stock solution was prepared to be 0.5 M in barbital and 0.5 M in NaOH. "Purified" grade Mallinckrodt barbital intended for pharmaceutical use was employed. (All chemicals used other than the barbital and the commercial flocculants were of reagent grade.)

To prepare the acid solution, measured amounts of the brine concentrate, buffer stock solution, and the amount of water needed to bring the final volume up to that desired were mixed in a beaker suspended in a boiling water bath. The beaker was temporarily covered with a watchglass and its contents allowed to heat up to above about 90°C. Next, the mixture was titrated with 0.5 M HCl to adjust the pH value to that desired in the synthetic brine. Finally, the amount of additional 0.5 M HCl needed to neutralize the sodium metasilicate solution, as determined by the earlier titration, was added to the beaker, and the resulting mixture was again allowed to heat up.

To start the reaction, the preheated alkaline solution was poured into the beaker containing the preheated acid solution with rapid stirring. The stirring was stopped after a few seconds, the pH measured, and periodic 1-ml samples withdrawn for analysis from then on.

Both dissolved silica and total silica were determined for by the molybdate yellow method. To determine the molybdate active (i.e., "dissolved") silica, the molybdate yellow method was employed directly. To determine the total silica (i.e., including the suspended colloidal silica), the specimen was first reacted with NaOH to digest and dissolve the colloidal silica. (Henceforth, "molybdate active silica" will be abbreviated as MAS, which should not be confused with MSA. MSA is molybdate active but so are some other small molecular and ionic silica species.)

The difference between the empirically determined molybdate active and total silica concentrations is approximately equal to the amount of colloidal silica suspended in the "brine." This "differential" technique is sensitive down to about $10 \text{ mg}\cdot\text{l}^{-1}$ suspended silica.

The measured silica concentrations reported in the figures and tables were not corrected for the effect of temperature. Therefore, the measured silica concentrations really are in units of $\text{g}\cdot\text{l}^{-1}$ at the stated temperature. To approximately convert these values to units of grams $(\text{kg}\cdot\text{H}_2\text{O})^{-1}$, multiply them by 1.05.

The sampling syringe was always preheated by rapidly drawing brine in and out of it once or twice before actually taking the sample to be analyzed.

The molybdate yellow method is subject to serious interference by the traces of dissolved silica and inorganic phosphate that are usually

present in tap water. To eliminate this problem, all solutions were prepared using water that was twice doubly deionized (DI) with mixed anionic/cationic ion exchange resins. The water coming out of our laboratory's DI water tap was already once doubly deionized; as a precaution, we sent it through our own column filled with mixed resins for the second double deionization step.

As in our previous work, we used the molybdate yellow procedure recommended by R. K. Iler (1979, p. 97). The molybdate reagent stock solution was prepared by mixing 100 g ammonium molybdate [(NH₄)₆ Mo₇ O₂₄ · 4H₂O], 47.0 ml concentrated NH₄OH (28% NH₃), and water to make 1.0 l of solution. The final working molybdate reagent solution was prepared by mixing 100 ml of the molybdate stock, 200 ml of 1.5 M H₂SO₄, and 500 ml DI water.

This working molybdate reagent solution was measured out in 40.0-ml aliquots and placed in 50.0-ml volumetric flasks. To determine dissolved silica, 1.0 ml of the solution to be analyzed was added to the molybdate reagent in the flask and the volume made up to 50.0 ml with DI water. The flask was then inverted and shaken three times, and the color allowed to develop for 3.5 minutes. (Shaking three times was found to improve the reproducibility of the results by ensuring more complete mixing.) The optical density was then measured at 400 nm using a double-beam spectrophotometer (Perkin-Elmer 550).

To determine total silica, a 1.0-ml aliquot was drawn and placed in a 50-ml plastic volumetric flask containing 1.0 ml of 1.0 N NaOH. The flask was stopped, shaken, and set in a hot water bath for 10 minutes to allow the colloidal silica to be digested by the NaOH. After the colloidal silica had been digested, 40.0 ml of the working molybdate solution and water to make the total volume up to 50.0 ml were added, and the procedure continued as described above.

In most of our experiments we treated the brine in one of two ways after 20 or 30 minutes had elapsed. One treatment was to increase the pH by adding NaOH. Another was to add a few mg·l⁻¹ of one of a number of commercial synthetic flocculants. In either case, the chemical addition was followed by a few minutes of rapid stirring. After stirring was stopped, pH was determined again and periodic sampling resumed.

We also considered the possibility that the rapid stirring itself, rather than the chemical addition that it accompanies, is what causes the colloidal silica to flocculate. This hypothesis was disproved by an experiment in which the brine was vigorously stirred for several minutes at the proper time without adding chemicals; this treatment was found to have no significant effect on the amount of silica that remained in suspension at the end of the experiment.

At the very end of the experiment the suspended silica remaining in the brine was determined by an "absolute" method. First, about 150 ml of the brine was decanted into a 200 ml beaker, being careful to leave as much of the

settled silica floc as possible behind. The decanted brine was held in a water bath at about 85°C for a few minutes to allow the small amount of coarse floc not removed by the first decantation step to settle out. Using a preheated 100-ml pipette, a 100-ml sample was then carefully withdrawn and placed in a preheated pressure filter funnel. Ordinarily, a 400-nm pore size polycarbonate membrane filter was used. The filter funnel was then sealed, and the fluid was driven through it with compressed nitrogen gas at about 1.3 bars gauge pressure.

The filter was then removed and placed in a plastic beaker with 3.0 ml of 1.0 N NaOH and heated in a boiling water bath for 10 minutes. After the silica was digested in this way, the filter was rinsed into the beaker and the contents of the beaker were then rinsed into a 50.0 ml volumetric flask containing 40.0 ml of the molybdate reagent for silica determination. Appropriate calculations then gave us the residual concentration of suspended silica in milligrams per liter of the "clarified" synthetic brine.

When implemented as described above, this technique can not be used to determine suspended silica concentrations greater than about 32 mg·l⁻¹, because higher concentrations cause the spectrophotometer to go off scale. This is why final suspended silica is reported as > 32 in Tables 2 and 3 for some experiments. However, high concentrations of suspended silica were usually obvious from the amount of floc accumulated on the filter. In such cases, the digested floc was diluted up to 50 ml with DI water, and then a 1-ml aliquot of this diluted solution was withdrawn, and the concentration of silica in it was determined in the usual way. This extra dilution step had the effect of extending the range of the method upward by a factor of 50.

In cases in which the brine treatment was apparently successful, the final suspended silica values were usually in the range of 2 to 5 mg·l⁻¹. These suspiciously repetitious values may be an artifact caused by slightly stirring up the floc during the second decantation step. Therefore, the amount of suspended silica remaining in the brine after a better executed settling process (as in a properly designed settling tank in a pilot or commercial-size brine treatment facility) may prove actually to be less than 3 mg·l⁻¹, all else being equal.

Of course, this method can only determine the concentration of particles and flocs large enough to be stopped by a 400-nm filter. In practice, this probably means all particles and flocs whose greatest linear dimension exceeds some size considerably smaller than 400 nm. Although the elemental colloidal particles are probably only between 20 and 100 nm in diameter under these conditions, the strongly flocculating nature of the treated brine probably ensures that most of the suspended silica is in the form of "flocs" large enough to be stopped by a 400-nm filter. Going to a finer filter did not seem warranted in the case of the laboratory tests, but probably would be in the case of pilot plant

experiments.

Sometimes we also determined the floc settling rate. This was done by remixing the floc with the brine after the filtration procedure, quickly pouring the mixture into a graduated cylinder, and measuring the rate at which the floc settled with a stopwatch. The values obtained in this way were only approximate, because the rate of sedimentation was strongly affected by convection currents and the like.

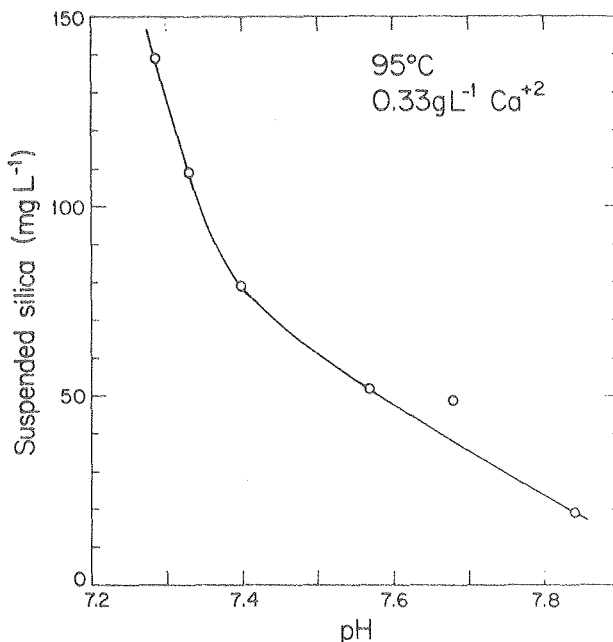
SILICA REMOVAL BY INCREASING pH

It is well established that increasing pH can destabilize colloidal silica suspended in salt solutions and cause it to flocculate or coagulate (Allen and Matijević, 1969, 1970, 1971; Matijević, 1973; Iler, 1975; Weres et al., 1980b, Sections 2.21 and 22). Increasing the pH increases the negative charge on the surface of the particles, and cations are adsorbed. These adsorbed cations serve as bridges between the particles, and this bridging effect is what causes the particles to adhere and flocculate. ("Coagulate" is probably more appropriate than "flocculate" in this particular case, but we use "flocculate" throughout this paper to be consistent with common usage in the water treatment field.) The flocculating ability of cations increases rapidly with their charge. In Cerro Prieto brines, calcium is probably the main flocculating ion.

In flashed Cerro Prieto brines the conversion of dissolved silica to colloidal silica is rapid, but removal of the colloidal silica from the brine by flocculation and settling is slow and incomplete. Therefore, the major task of preinjection brine treatment is to induce rapid flocculation and settling. Because Cerro Prieto brine contains a substantial amount of calcium, increasing the pH recommends itself as the simplest way to induce rapid flocculation.

Figure 1 semiquantitatively illustrates the effect of increasing the pH. In this experiment, the synthetic brine was originally constituted with a pH of about 7.3, and allowed to sit undisturbed for 25 minutes to let the concentration of MAS drop to a nearly steady-state value. Next, the brine was briefly stirred, the floc was allowed to settle for 2 minutes, and the first two 1-ml aliquots were withdrawn to determine the concentration of suspended silica by the differential method. Then a small amount of 1 N NaOH was added to increase the pH. After brief additional stirring the pH was measured, the floc was allowed to settle for 2 minutes without stirring, and two more aliquots were withdrawn for the determination of suspended silica. This cycle was repeated four more times to generate the rest of the points.

The data in Figure 1 are only semiquantitative in that the results obtained from such experiments are greatly affected by fine points of experimental design such as the duration of settling, and the size and shape of the reaction vessel. However, it is obvious from Figure 1



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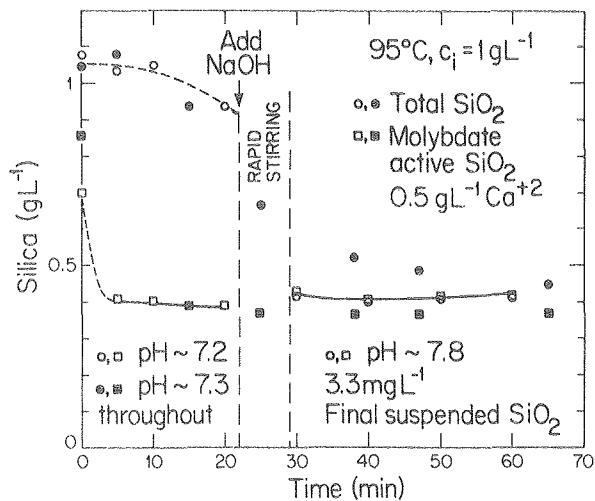
Figure 1. Suspended silica vs. pH. The pH of this synthetic brine was progressively increased by adding NaOH, and the suspended silica determined after each increase.

that at pH 7.3 flocculation is poor, and that increasing the pH to about 7.8 removes most of the colloidal silica from suspension.

The full, detailed data obtained in two typical "brine treatment" experiments are presented in Figure 2. In one of them (the solid symbols), the synthetic brine had an initial pH of about 7.3 and was maintained that way throughout the duration of the experiment. In the other (open symbols), the synthetic brine initially had a pH of about 7.2, and the pH was increased by adding a small amount of 1 N NaOH after 22 minutes. Except for the change in pH value and brief stirring in the second experiment, the two experiments were the same. The high Ca synthetic brine formulation was used in both.

In both cases, a substantial fraction of the silica had already polymerized by the time the first samples were taken for analysis. At this time there was also a faint white haze in the brine indicating the beginning of flocculation. (Unflocculated colloidal silica is invisible to the naked eye at these concentrations.) The very rapid initial stage of the polymerization reaction had been completed by the time of the second point, which was taken 5 minutes after the first. This means that a 5-minute "aging time" would probably suffice to polymerize the silica in a brine like this instead of the 22 minutes allowed in this experiment.

The 20-minute total silica values show that, by that time, the colloidal silica had flocculated to the point that it was beginning to settle.



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Figure 2. Synthetic brine flocculation experiments. Solid symbols: brine not "treated." Open symbols: pH increased after 22 minutes by adding NaOH. In this and further similar figures, silica concentrations are not corrected for temperature effect.

Flocculation and settling were slightly more pronounced in the synthetic brine that had the higher initial pH.

At 25 minutes the MAS concentration in the unmodified brine had already fallen to a "limiting" value. This value is somewhat higher than the equilibrium solubility level for bulk amorphous silica under these conditions which is about $0.33 \text{ g}\cdot\text{l}^{-1}$. (See Weres et al., 1980b, Sections 3.11 and 3.18 for detailed procedures to calculate the solubility of amorphous silica under various conditions.) That the value observed is higher than the "bulk solubility" value is due to the small size of the colloidal silica particles that are created under these conditions of rapid nucleation. Small particles are more soluble than bulk amorphous silica (AS), and their solubility determines the "limiting" MAS concentration.

Up to the point that the pH of the "treated" brine was increased, the MAS concentrations in the treated and untreated brines were equal. However, increasing the pH and stirring noticeably increased the MAS concentration in the treated brine. This is because increasing the pH increases the solubility of amorphous silica, from about 0.33 to about $0.35 \text{ g}\cdot\text{l}^{-1}$ in this case. That the post treatment MAS concentration was slightly above the corresponding equilibrium solubility value for bulk AS was again due to the greater solubility of small particles. If real, the apparent slow increase of MAS concentration in the modified brine toward the end of the experiment is probably due to continuing reequilibration of the colloidal silica with its chemically modified environment.

The partial redissolution of the colloidal silica during and, perhaps, after the flocculation process is a desirable phenomenon from the practical point of view. It means that if the clarified brine is separated from the floc quickly enough, the small amount of colloidal silica remaining in the brine will probably redissolve completely, if given enough time to do so. The final value of $3.3 \text{ mg}\cdot\text{l}^{-1}$ suspended SiO_2 was determined by the filtration technique. As discussed above, even this small value may be due to the difficulty of achieving good settling in a small container rather than to imperfect flocculation.

The MAS concentration at the end of this experiment was about $0.42 \text{ g}\cdot\text{l}^{-1}$, which is still above the equilibrium solubility of silica under the given conditions. This means that the brine will slowly deposit vitreous silica on any surface with which it comes into contact. Our best estimate of the molecular deposition rate, as calculated using the methods presented by Weres et al. (1980b, Section 3.14), is about $5 \mu\text{m}\cdot\text{yr}^{-1}$. This may or may not be small enough to avoid injectivity decline over the life of an injection well, depending on the pore size in the receiving formation and the extent of fracture permeability. It would not effect fracture permeability, but might damage pore permeability if the pores are small enough.

Other experiments have shown that the floc produced by increasing the pH settles at a rate of about $1 \text{ mm}\cdot\text{sec}^{-1}$, and that its volume after having settled for about 100 sec is about 10% of the initial total volume of the brine. Its volume would probably be considerably smaller if it were allowed to settle for a longer period of time, as would be the case in an actual settling tank.

Experiments with initial dissolved silica concentrations of 0.8 and $0.9 \text{ g}\cdot\text{l}^{-1}$ gave essentially the same results, except that the decline in MAS concentration to "steady-state" values required the full 20 minutes with the lower initial concentrations. (See Table 2.)

Similar experiments performed using the low Ca synthetic brine gave the same results. (See Table 3.)

In one experiment $0.05 \text{ g}\cdot\text{l}^{-1}$ of well-dispersed bentonite clay was added at the beginning. In spite of this, the treated brine was clear and the final suspended silica concentration was as low as usual. This suggests that the amorphous silica takes the clay particles with it when it flocculates and settles out. We conclude that this process may give brine that is completely free of all suspended solids, even if solids other than amorphous silica are initially present in it.

In these experiments sodium hydroxide was used to increase the pH as a matter of convenience. In practice, lime (calcium oxide or hydroxide) would be used because it is by far the cheapest base available. We estimate that only about $37 \text{ mg}\cdot\text{l}^{-1}$ of calcium hydroxide would be

TABLE 2. FLOCCULATION EXPERIMENTS WITH HIGH Ca SYNTHETIC BRINE

Date	Flocculant	Quantity used	Initial SiO ₂	Initial pH	Suspended SiO ₂ at (30 min.) (40 min.)		Final suspended SiO ₂	at (min.)
12/12/78	none	-	1000	7.40		151 [†]	5.6	>96
12/11/78	none	-	1000	7.17	321		3.9	>100
2/ 2/79	pH raised	to 7.77	800	7.41	459*	20	3.9	>50
12/19/78	pH raised	to 7.79	800	7.18	<10	<10	1.7	>70
1/ 5/79	pH raised	to 7.74	900	7.29	44	15	3.3	>60
12/21/78	pH raised	to 8.01	900	7.12	460*	27 [†]	3.5	>48
12/13/78	pH raised	to 7.75	1000	7.24	15	<10	3.3	>60
6/11/79	MF 572C	2 ppm	1100	7.23	69 [†]		>34	>33
5/30/79	MF 572C	2 ppm	1100	7.20	<10		5.0	>30
1/10/79	MF 573C	1 ppm	1000	7.25	449*	36	2.4	>50
1/ 9/79	MF 573C	2 ppm	1000	7.27	576*	<10	1.0	>60
4/27/79	MF 573C	5 ppm	900	7.27	<10 [†]		4.0	51
1/ 8/79	MF 585C	5 ppm	1000	7.17	34	13	1.8	>50
6/12/79	MF 591C	2 ppm	1100	7.33	60 [†]		>32	>32
12/20/78	MF 1563C	2 ppm	800	7.09	295*	26	5.3	>60
12/18/78	MF 2535C	2 ppm	1000	7.23	64	31	13	>67
2/ 7/79	MF 836A	2 ppm	1000	7.34	78	58	28	>60
2/ 6/79	MF 836A	20 ppm	1000	7.25	39	40	22	>50
4/30/79	Calgon M 503	5 ppm	1100	7.31	18		3.0	>30

Notes: Silica concentrations in ppm; 1 ppm = 1 mg·l⁻¹; MF = American Cyanamid Magnifloc

*Point taken before "treatment"

†Point taken within 5 min. of stated time rather than at exactly that time.

TABLE 3. FLOCCULATION EXPERIMENTS WITH LOW Ca SYNTHETIC BRINE

Date	Flocculant	Quantity used	Initial SiO ₂	Initial pH	Suspended SiO ₂ at 30 min. 40 min.		Final suspended SiO ₂	at (min.)
4/13/79	none	-	1094	7.24	253	179	27	>60
4/10/79	none	-	1000	7.26	356	294	32	>60
4/11/79	pH raised	to 7.90	1000	7.29	<10 [†]		2.5	>34
4/17/79	pH raised	to 7.83	1094	7.30	<10		3.6	>30
5/31/79	MF 572C	2 ppm	1100	7.22	617*	243 [†]	177	>45
6/ 4/79	MF 572C	2 ppm	1100	7.34	530*	31	26	>40
6/ 1/79	MF 572C	2 ppm	1100	7.32	278		303	>30
4/24/79	MF 573C	2 ppm	900	7.28	388 [†]		310	65
4/18/79	MF 573C	2 ppm	900	7.27	499* [†]		32	52
6/ 5/79	MF 577C	2 ppm	1100	7.36		79 [†]	>32	>36
4/16/79	MF 585C	2 ppm	1094	7.32	<10 [†]		31	>30
6/ 5/79	MF 587C	2 ppm	1100	7.32	94*		>32	>31
6/ 6/79	MF 591C	2 ppm	1100	7.31	295*		27	>34
5/ 1/79	Calgon M 570	5 ppm	1100	7.25	92		133	>31
5/ 2/79	Calgon M 580	5 ppm	1100	7.23	599 [†]	144 [†]	82	>45
5/ 2/79	Calgon M 590	5 ppm	1100	7.30	149		174	>30
4/12/79	Purifloc C31	2 ppm	1000	7.27	58 [†]		30	>32
4/20/79	Separan CP7	2 ppm	900	7.25	503 [†]		338	>28
4/19/79	Separan CP7	2 ppm	900	7.41	230* [†]	55 [†]	0.7	>44
4/11/79	Separan CP7	2 ppm	1000	7.37	39 [†]		24	>33
5/ 1/79	Separan CP7	5 ppm	1100	7.30	18* [†]		21	>28
4/25/79	Separan CP7	7 ppm	1000	7.27	170 [†]		>31	>35

Notes: Silica concentrations in ppm; 1 ppm = 1 mg·l⁻¹; MF = American Cyanamid Magnifloc

Purifloc and Separan are Dow products

*Point taken before "treatment"

†Point taken within 5 min. of stated time rather than at exactly that time.

needed to raise the pH to 7.8 (see Iglesias and Weres, 1980).

Rothbaum and Anderton (1975) have pilot tested a process for removing both suspended and dissolved silica from the brines at Wairakei and Broadlands, New Zealand, by adding a large amount of lime to them (up to 700 ppm CaO). The silica was precipitated out as an amorphous calcium silicate. Adding lime in quantities as small as those proposed here apparently was not effective in flocculating the suspended silica because the brines in these two fields are of much lower salinity than that at Cerro Prieto, and contain much less calcium. Sodium hypochlorite was also added to the brines, and this caused the arsenic in it to precipitate out with the silica. All in all, this is basically a different process from the one proposed here.

EFFECT OF SYNTHETIC FLOCCULANTS AND SUMMARY

Cationic polymers are known to be effective flocculants of colloidal silica. So are quaternary amines with long side chains (general formula: $NR_4^+X^-$). For a discussion of the general principles involved, see Iler (1973, p. 53-63; 1979, p. 384-396).

A variety of synthetic organic flocculants were obtained from three manufacturers and tested. The results of these experiments are summarized in Tables 2 and 3. The flocculants tested are listed and briefly described in Table 4. The detailed results of a synthetic brine experiment with a synthetic flocculant are presented in Figure 3.

TABLE 4. SYNTHETIC FLOCCULANTS TESTED

Manufacturer	Product	Chemical nature
American Cyanamid	Magnifloc 572C	Probably a polymeric quaternary ammine.*
"	" 573C	do.
"	" 577C	do.
"	" 585C	do.
"	" 587C	do.
"	" 591C	do.
"	" 1563C	Cationic polymer; otherwise unknown.
"	" 2535C	do.
Calgon	M503	Cationic polymer; otherwise unknown.
"	M570	do.
"	M580	do.
"	M590	do.
Dow	Separan CP7	Probably a cationic polyacrylamide.†
"	Purifloc C31	do.

*The American Cyanamid product literature did not identify the chemical nature of their products. However, the Magnifloc 500C series products are stated to be of low molecular weight, and a shipping label on a package of samples we received identified the contents as quaternary ammonium compounds.

†The Dow product literature stated that most of the products in the Separan and Purifloc series belong to this chemical class.

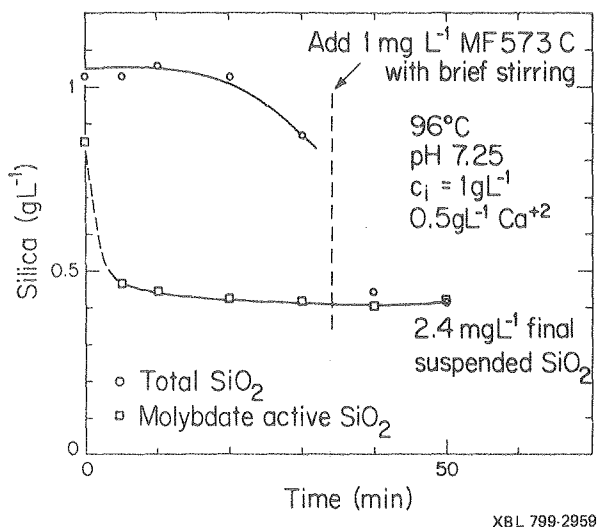


Figure 3. Synthetic brine flocculation experiment. High-Ca synthetic brine. Effect of Magnifloc 573C.

The experiments in this series were like those discussed above in the section on silica removal by increasing pH, with one exception. The requisite amount of the synthetic flocculant was added to the synthetic brine with stirring after about 30 minutes instead of adding NaOH.

The most important data in Tables 2 and 3 are the final suspended silica values determined at the end of the experiment by the filtration method, but these values cannot be considered in isolation. The final suspended silica values for the first two experiments in Table 2 ("untreated brines") are low, but only because of the abnormally long time that these experiments were allowed to run. A treatment time this long would probably not be acceptable in practice. The 30- and 40-minute suspended silica values determined by the differential method are high, and the slow, steady decline of suspended silica concentration in the second experiment is shown in Figure 2 (solid symbols). The suspended silica concentrations in "untreated" low-Ca synthetic brines likewise did not drop to acceptable values in a reasonable time (Table 3).

Raising the brine pH to about 7.8 quickly reduced the suspended silica concentration and gave a final value below $5 \text{ mg} \cdot \text{l}^{-1}$ in all cases, both with the high- and low-Ca synthetic brines (Tables 2 and 3 and Fig. 2).

With the high-Ca synthetic brine, several of the synthetic flocculants gave generally promising results. Magnifloc 573C appears to be the most promising of them. Of the flocculants tested with the high-Ca synthetic brine, only Magnifloc 836A, which is an anionic polymer, was confirmed to be definitely ineffective.

As is evident from Table 3, synthetic flocculants in the concentrations used did not give good results with the low-Ca synthetic brine. The one low final suspended silica value obtained with Dow Separan CP7 was probably anomalous, because we were unable to reproduce it despite four attempts to do so. Some of the entries in Table 3 do, however, suggest that at least some of the synthetic flocculants cause a significant decrease in suspended silica concentration, even though the final values were still unacceptably high. These flocculants might have been more effective if added in larger amounts, but such a treatment would not be practical given the relatively high price of these products and the very large amount of water that needs to be treated.

We were unable to explain the difference in effectiveness of the synthetic flocculants with the two different synthetic brines. Nor were we able to correlate it with any particular chemical difference between the two synthetic brine compositions.

The advantages of using synthetic flocculants in practice would be:

1. Relatively small amounts are used.
2. The only preparation they need prior to use is dilution with clean water to about 1% concentration.
3. They cannot cause the precipitation of carbonate minerals as increasing the pH might.

Their disadvantages are:

1. Most of them are expensive.
2. They slowly decompose, especially at high temperature.
3. They do not increase the solubility of silica as lime does.
4. They are specialty products that might not be conveniently and reliably available for use at Cerro Prieto.

The advantages of using lime are:

1. It is very cheap and universally available.
2. It increases the solubility of silica in the treated brine.

The disadvantages of using lime are:

1. Increasing the pH might induce the precipitation of carbonate minerals (see Iglesias and Weres, 1980) or of an amorphous calcium silicate phase.
2. The equipment used to produce lime milk or gel from quicklime is somewhat complicated and expensive.

FIELD VERIFICATION OF LABORATORY RESULTS

A few experiments were performed at Cerro Prieto to confirm the laboratory results. These experiments were essentially the same as those discussed above, except that freshly collected samples of actual geothermal brine were used instead of synthetic brine. Also, when the brine pH was raised, a nearly saturated solution of calcium hydroxide was used for this purpose instead of sodium hydroxide.

These experiments were performed at the CFE Laboratory at Cerro Prieto with the help of J. J. Fausto L. of CFE. Brine from Cerro Prieto wells M-14 and M-30 was used because these wells are near the laboratory. The brine from M-30 is considered to be more representative of the field as a whole.

Wells M-14 and M-30 are both producing wells that were steadily producing steam and brine when these experiments were performed. These wells (and all others at Cerro Prieto) have a special, small-diameter, brine-sampling line and miniature Webre separator connected to the wellhead. When this system was first turned on, brine was allowed to flow through it for at least 20 minutes before sampling. The sample was collected in a vacuum bottle, which had first been rinsed with hot brine three times to bring it up to brine temperature. Immediately after taking the sample the time and temperature were recorded, and the first two 1-ml aliquots for the determination of total silica and MAS were withdrawn and put into prepared plastic 50-ml flasks that contained sodium hydroxide and ammonium molybdate reagent, respectively. The sample was then rushed to the laboratory by car. The time from sampling to laboratory was usually about 8 minutes. At the the laboratory, the whole sample was poured into a prepared beaker in a hot water bath, and two more 1-ml aliquots were withdrawn for silica analysis.

The colloidal silica that formed in the brine taken from M-30 usually began to flocculate and settle by the time that the brine was poured into the beaker. However, the amount of colloidal silica that remained in suspension after 30 minutes ($>10 \text{ mg}\cdot\text{l}^{-1}$) probably would not be acceptable for reinjection. Figure 4 shows how well adding lime water to M-30 brine removes the suspended silica. Adding $2 \text{ mg}\cdot\text{l}^{-1}$ of Magnifloc 573 to M-30 brine

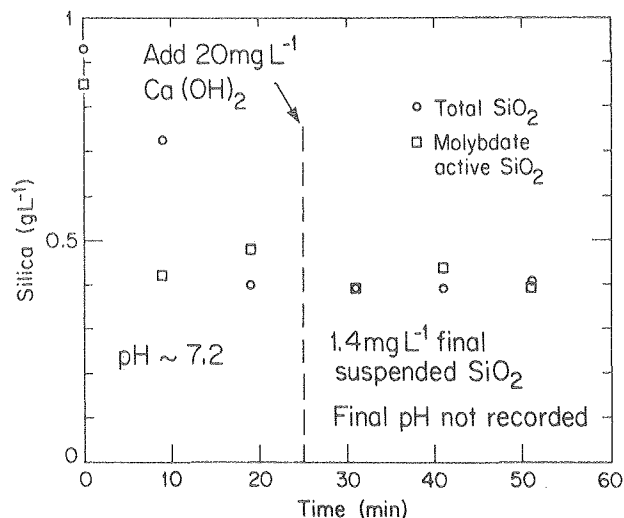


Figure 4. Experiment performed at Cerro Prieto using freshly flashed brine from well M-30.

did not reduce the suspended silica to acceptable levels. (The results of these experiments are not shown here.)

The colloidal silica in unmodified brine from M-14 does not flocculate even after the brine has been incubated for one hour. Figure 5 shows this and the effect of adding a small amount of lime water to M-14 brine. This small amount of lime was added by mistake, but there was no chance to repeat the experiment using more lime. Even this small amount of lime caused most of the colloidal silica to flocculate and settle out. Adding more lime, say $30 \text{ mg}\cdot\text{l}^{-1}$, would probably reduce the suspended silica in M-14 brine to acceptable levels. The very small difference between the pre- and post-treatment pH values in Figure 5 is probably due to experimental error.

Adding $2 \text{ mg}\cdot\text{l}^{-1}$ of Magnifloc 573C to M-14 brine did reduce the suspended silica concentration to an acceptable level (Fig. 6).

The volume and quality of the data we obtained in the field was reduced by the difficulty of working in an unfamiliar laboratory and time constraints. However, the results obtained do seem to confirm the results of the laboratory work. Increasing the pH seems to work with brine from either well, while Magnifloc 573C works only with brine from M-14; this is exactly the same pattern as that observed working with the two different synthetic brines.

RECOMMENDATION FOR A PILOT PLANT TEST

We doubt that bench tests with either synthetic brines or samples of real brine can profitably be carried much further. The results reported here are probably about as complete and convincing as can be obtained in this way, given

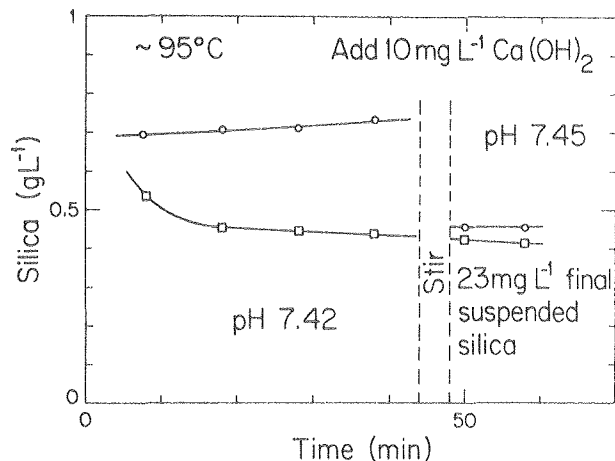


Figure 5. Laboratory test at Cerro Prieto using brine from well M-14. One or both pH values may be in error.

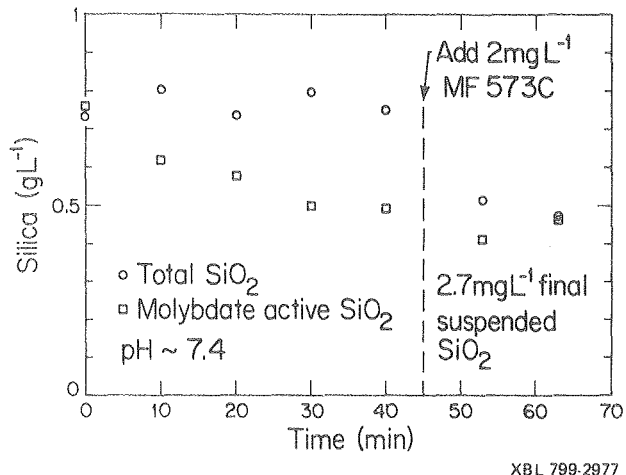


Figure 6. Laboratory test at Cerro Prieto. Effect of Magnifloc 573C on brine from well M-14.

the intrinsic limitations of bench tests and the variability of natural brines. Further progress will only come from pilot plant experiments in the field at Cerro Prieto.

Figure 7 is a schematic diagram of a pilot plant that would allow the brine treatment processes suggested by the results of our bench tests to be evaluated in a practically meaningful way. A design flow rate of 5 to 10 m³·hr⁻¹ would probably be most convenient to work with. This pilot plant resembles the one used by Rothbaum and Anderton (1975).

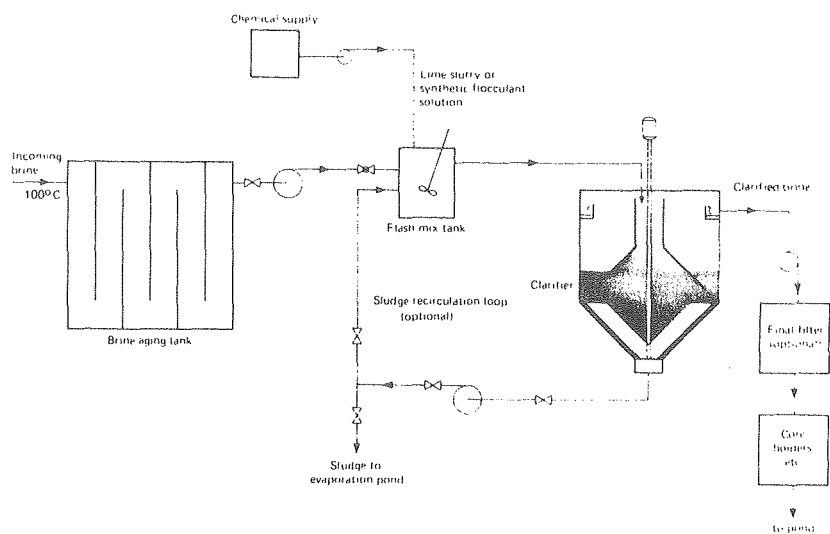


Figure 7. Recommended brine treatment pilot plant facility for Cerro Prieto.

When operated without sludge recirculation, this pilot plant would closely reproduce the processes evaluated in our bench tests. As in the bench tests, the function of the brine aging step is to allow time for the dissolved silica to be converted to colloidal silica. However, partial flocculation and settling of colloidal silica in the aging tank could lead to problems with sludge accumulation there. If this proves to be a serious problem, the "aging step" could be replaced by recirculation of part of the sludge coming out of the clarifier. The large amount of colloidal silica in the sludge would react with the dissolved silica in the brine and decrease the dissolved silica concentration in the resulting mixture to its steady-state value almost instantaneously. Sludge recirculation for this purpose is considered to be essential at Niland, California, because of the rather low rate of silica polymerization in the brine there (Quong et al., 1978). However, at Cerro Prieto the rate of silica polymerization is high enough for brine aging to be a reasonable alternative. As little as 5 minutes of aging might be enough.

When this pilot plant is operated without sludge recirculation, scale is most likely to form in the brine inlet pipe and the part of the aging tank nearest to it. The aging tank should be designed with this in mind. For example, it might be possible to design it in such a way that the incoming brine does not come into contact with any part of the tank until a few minutes after it enters the tank and is already relatively nonreactive.

The sketch of the brine aging tank in Figure 7 is meant to be a view from the top. The brine flows from side to side around vertical baffles.

A vertical laminar flow tank without baffles, which the brine enters at the top and leaves at the bottom, is another possibility. All that is really required is that the aging tank provide approximately plug flow reactor conditions, that sludge not accumulate in it, and that it be easy to clean.

In Figure 7, the clarifier, mixing tank, and sludge recirculation loop are shown as separate components. If a process that includes sludge recirculation were to be ultimately implemented, all three of these components could be replaced by a reactor-clarifier, which combines the functions of all three in a single unit. Even if sludge recirculation is not required, there are clarifiers available that incorporate the function of the mixing tank as part of the clarifier. The "separate component" configuration shown in Figure 7 is recommended for the pilot plant because it allows maximum experimental flexibility and clearest separation of the effects of the various components on the overall performance of the process.

The pilot plant will require a dual chemical feed system to allow both pH increase and synthetic flocculant addition to be evaluated. The feed system for the synthetic flocculant need consist only of a storage tank for the flocculant solution and a metering pump.

In a full scale brine treatment facility pH would be increased by adding a hydrated lime slurry or gel to the brine. The slurry or gel would most likely be produced on the spot by hydrating quicklime in an appropriate reactor. However, this would be completely impractical to implement on the small scale of the pilot plant. An infinitely simpler and more convenient method to generate a hydrated lime slurry would be to mix metered solutions of NaOH and CaCl_2 just before they enter the mixing tank. This would produce a suspension of $\text{Ca}(\text{OH})_2$ in NaCl solution. Suitable experiments performed in our laboratory indicate that $\text{Ca}(\text{OH})_2$ scaling at the point of mixing would not be a problem. It would be even simpler, but less realistic, to use NaOH alone to increase the brine pH in the pilot plant tests.

We doubt that a final brine filtration step will prove necessary at Cerro Prieto, but it would be desirable to have that option available during the pilot plant work.

The floc produced by the processes discussed in this report is mostly water, and may actually represent as much as 5 to 10% of the total volume output.

Drawing on related practical experience of Quong et al. (1978) at Niland, we recommend the following instrumentation and tests for monitoring the performance of the process:

1. A flow-through turbidimeter is needed to monitor the turbidity of the "clarified" brine. This instrument would allow suspended silica concentrations above about $10 \text{ mg} \cdot \text{l}^{-1}$ to be instantly

detected and continuously monitored in a semi-quantitative way. This capability would be very helpful in "coarse tuning" the operation of the pilot plant.

2. Some of the "clarified brine" should be pumped through a membrane filter. The filtration equipment should include a precise constant flow rate pump and instrumentation for continuous monitoring of the pressure drop across the filter. This equipment would allow the "formation plugging potential" of the clarified brine to be determined via the method of Barkman and Davidson (1972).

3. The solid residue that collects on the filter should be analyzed to quantitatively determine the concentrations of suspended silica and calcium carbonate in the brine. For details of these techniques see the section on experimental methods above, and Weres et al. (1980a, Appendix 2), respectively. There is no lower limit to the concentration of suspended solids that can be measured in this way. Simply flow enough brine through the filter to accumulate the amount needed for convenient analysis; this is typically only a few milligrams.

4. Clarified brine should be pumped through a sandstone core that is representative of the reservoir. The core holder should be instrumented to allow the permeability to be followed continuously as with the membrane filtration apparatus. High core confining pressure is not needed; a simple Hassler sleeve-type core holder immersed in a boiling water bath would be completely adequate.

5. Cores used in the core-flushing experiments should be sectioned and studied petrographically afterwards.

6. Appropriate provision should be made to sample all streams in the pilot plant for analysis. Total silica, MAS and pH should be measured at all points, and complete mass balances determined. The brine aging tank and clarifier should each be provided with several sampling ports.

7. Corrosion monitoring coupons should be distributed throughout the system.

8. Quartz glass coupons should be distributed throughout the system to determine scale deposition rates. The use of quartz glass coupons would allow the scaling rates to be quickly and quantitatively determined without the complicating effects of simultaneous corrosion processes. The weight increases of the coupons would give the rates of scale deposition, and scale morphology could be determined by examining the specimens microscopically. (Laboratory experiments analogous to this are discussed below.)

Both in the pilot plant and in the ultimate practical system, all equipment should be designed to keep air out of the system. Steam jacketing the major vessels is recommended for this purpose. Particular efforts should be made to control heat loss from the small and complex clarified brine testing system discussed above.

SCALE DEPOSITION FROM SYNTHETIC BRINES:
EXPERIMENTAL METHODS

Extensive solid and semisolid deposits of nearly pure colloidal amorphous silica form throughout the existing waste water disposal system at Cerro Prieto. Field experiments with low-pressure (i.e., second-stage) steam separator units have shown that rapid deposition of amorphous silica scale occurs within the separators if they are operated with an exiting brine temperature below about 130°C. This scale is solid and forms at a rate of up to about 1 mm·day⁻¹ (R. Hurtado J., private communication and scale samples, 1978). These deposits consist of colloidal amorphous silica that has been more or less cemented by the molecular deposition of dissolved silica between the particles. (See Weres et al., 1980a, Section 10.)

Silica scaling is presently only a minor problem at Cerro Prieto because the existing very simple waste-water disposal system is not sensitive to it. However, second-stage steam separators are, and a preinjection brine treatment system would be as well. Therefore, the kinetics of scale deposition and possible control methods are of interest. These things may be studied in the laboratory using synthetic brines precisely because scaling rates at Cerro Prieto are high enough to be conveniently measurable.

For scaling rate data to be meaningful, the scale must be deposited under steady state chemical conditions. This is clearly not possible in a "beaker test" like those discussed above, and a continuous-flow kinetic system must be used.

The system developed for this experiment is schematized in Figure 8. The compositions of the

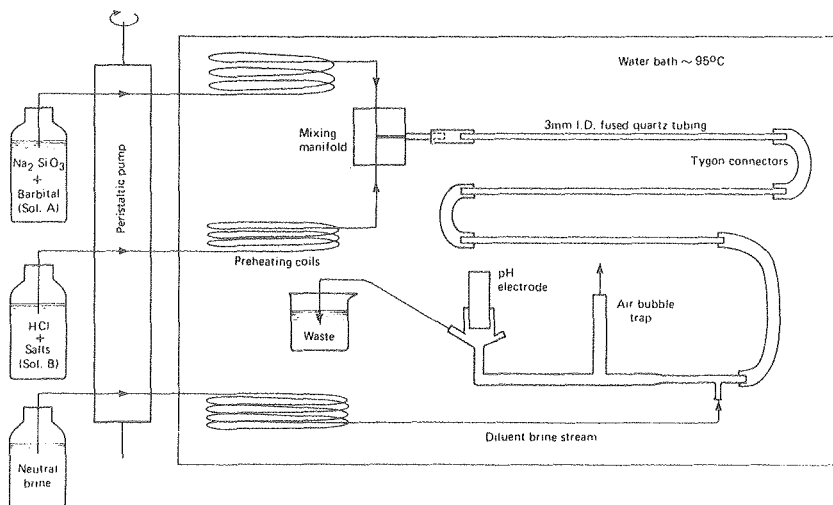
three solutions employed in most of these experiments are presented in Table 5, as well as the composition of the synthetic brine that is formed when two of them are mixed. This synthetic brine has the same calcium concentration as does the high-Ca brine in Table 1, and the same sodium, potassium, and boron concentrations as the low-Ca synthetic brine in Table 1. It differs from both of the synthetic brines in Table 1 in that the concentration of barbitol in it is 2-1/2 times higher.

The three solutions were pumped at equal rates by separate cassettes on a 10-channel Manostat Cassette pump. The cassettes were attached to the low speed-drive shaft of the pump, and 1.5-mm I.D. soft Tygon tubing was used. In most of the experiments the flow rate of each solution was 23 ml·hr⁻¹, and the total synthetic brine flow rate was 46 ml·hr⁻¹.

The whole kinetic system was immersed in a hot water bath whose temperature was nearly constant at about 95°C. All of its components were compactly mounted on a supporting rack made out of silver soldered 3-mm brass rod. The maximum dimensions of the rack were about 26 x 16 x 16 cm.

After leaving the pump, the three solutions flowed through 1-m-long heat-exchange coils made out of thin-walled Teflon tubing with an inner diameter of about 1 mm.

The synthetic brine was "constituted" and the silica polymerization and scale deposition reactions were initiated by mixing (preheated) solutions A and B in a mixing manifold made out of a Teflon block. Plugging of the mixing manifold by semisolid silica deposits was a recurrent problem. This problem was ultimately reduced to



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Figure 8. Synthetic scale deposition apparatus. There are actually four lengths of quartz glass tubing, each of them consisting of several short segments that are held together by Tygon connectors. An early version of the "pH electrode manifold" is shown here.

TABLE 5. SOLUTIONS USED IN SCALE DEPOSITION EXPERIMENTS

	Solution A		Solution B		Final synthetic brine		Neutral brine	
	(ppm)	(mM)	(ppm)	(mM)	(ppm)	(mM)	(ppm)	(mM)
SiO ₂	2,000	33.3			1,000	16.7		0
Na From Na ₂ SiO ₃	1,530	66.6						
From NaBarb.	2,299	100						
From NaCl			9,389	498.4				
Total Na	3,829	166.6			6,610	288	6,610	288
K			2,872	74	1,436	37	1,436	37
Ca			1,002	25	501	12.5	501	12.5
B			26.2	2.4	13.1	1.2	13.1	1.2
Barbital		100				50		0
HCl To neut. sil. st.				66.6				
To adj. pH				11.8				
Total HCl				78.4				
Total Cl			21,655	610.8	10,827	305.4	12,409	350

manageable proportions by (1) reducing the silica concentration in the synthetic brine to 1.0 g·l⁻¹ and (2) drilling out the exit channel of the mixing manifold to about 2 mm I.D. Even so, the experiment often ended when the mixing manifold plugged up and one of the upstream tubing connections "popped" to relieve the pressure. Careful operator attention was needed to accurately note the time at which this happened, so that the total reaction time could be determined.

The scale was actually deposited inside of 3-mm I.D. fused quartz tubing. This material was chosen because it is very nearly chemically identical to the silica scale being deposited. Therefore, the rate of deposition inside these tubes should not be very different from the rate of deposition on preexisting scale deposits; i.e., it should closely approach the "steady state" deposition rate, despite the very small amount of silica scale actually deposited during a typical experiment.

The fused quartz tubing "run" typically consisted of 10 short segments with a total length of 67 cm. Before the experiment, the cut ends of each segment were fire polished, and the segments were rinsed thoroughly with DI water and dried. Then they were "coded" with indelible ink for identification, and carefully weighed with an

electronic balance to ± 0.1 mg. These short segments were assembled into four straight "lengths" by joining them with short pieces of soft Tygon tubing slipped over the ends. The ends of the segments within each length were brought together snugly within these Tygon connectors so that the fused quartz tubing within each length was essentially continuous.

One segmented length of 15 cm and two of 20 cm, and one continuous length of 12 cm were used. (Only three lengths are shown in Figure 8 and their segmented nature is ignored for simplicity.) These particular lengths were chosen for convenient assembly and handling. The straight lengths are connected by longer pieces of soft Tygon tubing, which is also used for connections elsewhere in the system. The Tygon tubing used for this purpose has an inner diameter of about 2-1/2 mm. The length of the flow path through each of the longer Tygon connectors between the lengths of quartz glass tubing was 5 cm.

All joints between the longer Tygon connectors and glass or Teflon tubing were reinforced by wire ties wound around them. Also, the supporting rack was carefully designed to minimize forces on the connectors. These precautions were

necessary because Tygon softens in hot water and the connectors would have frequently slipped off otherwise.

The total length of the quartz glass tubing and Tygon connectors was 82 cm. At a brine flow rate of $46 \text{ ml}\cdot\text{hr}^{-1}$, this gave a total transit time of about 7.1 minutes.

After leaving the quartz glass tubing, the synthetic brine flows through a glass manifold that holds the tip of a pH electrode. Before it enters the electrode compartment, the synthetic brine is diluted by one-third with the "neutral brine." This solution is the same as the synthetic brine except that it does not contain any silica or barbital (see Table 5). The purpose of diluting the brine at this point is to reduce the concentration of dissolved silica and, thereby, avoid silica deposition on, and damage to, the glass membrane of the electrode. The neutral brine used for this purpose was formulated to resemble the synthetic brine in order to minimize the change in pH caused by dilution.

An "inverted T" was built into the manifold to remove bubbles from the brine before it reached the electrode. This was necessary, because bubbles of steam and air inevitably formed in the solutions during preheating, and caused wild fluctuations in the pH reading if allowed to reach the electrode compartment. Both the main longitudinal member of the manifold and the air vent were made out of 3-mm I.D. glass tubing. A smaller air vent diameter would have caused "burping," and the tube it was joined to could not have a smaller diameter than the vent.

The brine flowed into the electrode chamber through the bottom, up past the electrode's glass bulb, and out through a side port. In early versions of the manifold, another side port was provided for a thermoelectric temperature sensor which directly read the brine temperature (rather than the water bath temperature). Brine temperature monitoring was abandoned after it was established that it was never more than 1°C lower than the water bath temperature, and the second side port was eliminated from later versions of the manifold. The annulus around the electrode was sealed off with two O-rings.

Maximizing the time resolution of the pH reading requires that the volume of the manifold be minimized by careful design. Its longitudinal member was only 8 cm long, and we were able to achieve a time resolution of about one minute in the pH reading.

Devising adequate means of controlling and monitoring brine pH presented the major challenges in developing this technique. Some degree of varying mismatch between the pump channels pumping solutions A and B is inevitable. Because these solutions contain substantial concentrations of base and acid, respectively, pumping irregularities cause fluctuations in the pH of the resulting synthetic brine. Also, it was not possible to put the barbital in with the acid and salts and to "pretitrate" it because the constituent solutions were prepared and kept at room temperature;

attempts to do so inevitably caused precipitation of the sparingly soluble acid form of barbital. This is why a higher concentration of barbital was needed here than in the "beaker experiments" discussed above, and why pH had to be continuously monitored.

A Lazar sealed pH electrode was used in this work. The pH electrode was allowed to preheat before the start of the experiment. It was calibrated by pumping a commercial standard pH 7 buffer solution (Mallinckrodt Buffer) through all three pump channels. After a stable signal had been achieved, the meter was set to the pH of the buffer at the bath temperature. The tubes were then rinsed off with water and set in the reactant and diluent solutions. Leaving a bubble in each of these feed lines allowed the operator to follow the position of the reactants and note when they met in the mixing manifold. After the reactant solutions reached the mixing manifold the pump was adjusted to give the desired flow rate of $23 \text{ ml}\cdot\text{hr}^{-1}$ per channel.

A typical experiment ran for 1-1/2 to 2 hours. At the end of the experiment, the reaction tubes were removed and rinsed thoroughly to remove any loose silica. They were placed in an oven set at 110°C and allowed to dry overnight. When dry, they were weighed; the difference in weight before and after the reaction was the amount of silica deposited, which was usually a few milligrams per segment.

In a typical experiment, about 75 ml of synthetic brine containing a total of about 75 mg of SiO_2 flowed through the system. About 10 mg of this was typically deposited inside the quartz glass tubing. An unknown but probably much smaller amount was deposited inside the Tygon connectors. Because only about 10 to 15% of the total silica in the brine was deposited, it seems unlikely that the relatively large surface-to-volume ratio of the tubes significantly affected the results.

SCALE DEPOSITION: EXPERIMENTAL RESULTS

A total of about 20 scale deposition experiments produced usable results. The range of brine pH values in these experiments was 6.95 to 7.50.

The values obtained for scaling rate vs. position along the flow path for four experiments at pH near 7.35 are presented in Figure 9. Each point represents the average scaling rate within a segment of quartz glass tubing determined by dividing its weight gain by the product of its inside surface area and the duration of the experiment. The "distance along tube" is the distance along the flow path, including the Tygon connectors, measured from the beginning of the first tube segment. (The three connectors start at about the 15, 40, and 65 cm positions, respectively.) The symbol representing the scaling rate in a given tube segment is plotted at the position of the midpoint of that segment. Each value is the average of the deposition rate over the whole length of the given segment. The zero of the time scale is slightly offset from

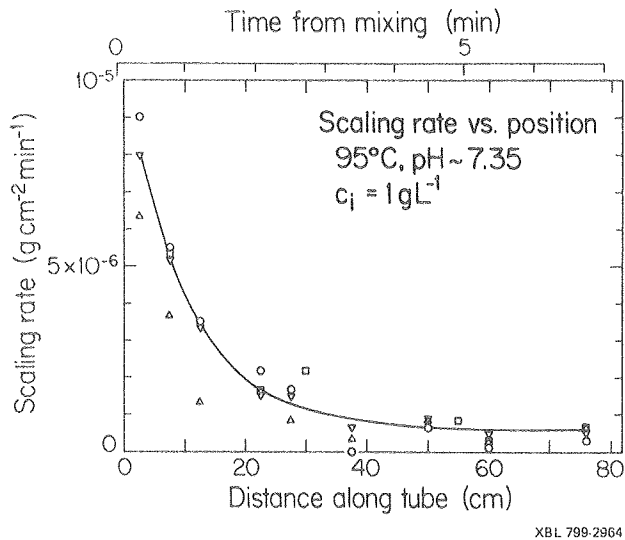


Figure 9. Experimentally determined scale deposition rates as a function of position along the quartz glass tube and the time from mixing.

that of the distance scale to account for the 7-second transit time between the point of mixing and the start of the quartz glass tubing.

The dissolved silica concentration as a function of position along the tube is unknown. This means that the rate of molecular deposition cannot be calculated. [By "molecular deposition" we mean the deposition of dissolved silica onto a solid surface one molecule at a time. See Weres et al. (1980b) regarding the nature and kinetics of this process.] However, it is easy to determine that the rate of scale deposition is one or two orders of magnitude greater than the rate of molecular deposition of dissolved silica under similar conditions. This demonstrates that the dominant mechanism of scale formation under these conditions involves deposition onto the tube wall of colloidal silica formed in the liquid phase.

The deposition rate is high at first and drops off rapidly with time and distance along the tube. Comparing this data with the curves of MAS vs. time presented in Figures 2 and 3 shows that the decrease in scaling rate is roughly parallel to the decrease in dissolved silica concentration. Because only a modest fraction of the colloidal silica that is formed in the brine is deposited as scale, the decrease in colloidal silica suspended in the brine with time cannot be the cause of the rapid drop-off in the deposition rate. We conclude the rate of molecular deposition must control the overall scaling rate under these conditions.

Almost certainly, the first step of scale deposition involves the attachment of colloidal silica particles and "clumps" formed in the liquid phase to the tube wall by electrostatic forces identical to those that cause flocculation in the liquid phase. The particles are then

permanently attached and the deposit made solid by molecular deposition of dissolved silica between the particles. This model was originally proposed by Iler (1973).

Practically speaking, Figure 9 shows that aging newly flashed brine for 3 to 5 minutes should suffice to greatly reduce the scaling rate further along in the system.

Figure 10 shows the effect of pH on the deposition rate in the first three tube segments. Between pH 6.95 and 7.35, the effect of pH on the deposition rate is comparable to its effect upon the rate of molecular deposition under similar conditions (see Weres et al., 1980b, Figure 3.4 or Table A3.2). This means that the trend can probably be meaningfully extrapolated to at least moderately lower pH values. No experiments at pH values below 6.95 were attempted because of the inconveniently low scaling rates in this range. Also, such work would have required a different buffer system--probably barbital and maleate or maleate alone--with all the additional developmental effort and risk of inconsistent results that would have entailed. The unexpectedly lower deposition rates obtained in the one experiment at pH 7.50 may or may not be correct; they were not verified.

Figure 10 suggests that even a moderate pH decrease may be effective in controlling silica scale deposition. For example, extrapolating the trend to pH 6.5 suggests that at this pH the deposition rate will be only about one-fourth of that at pH 7.35. This is discussed further by Iglesias and Weres (1980).

Scanning electron micrographs of synthetic silica scale formed in our experiments and scale specimens collected in the field at Cerro Prieto are presented and discussed in Section 10 of Weres et al. (1980a).

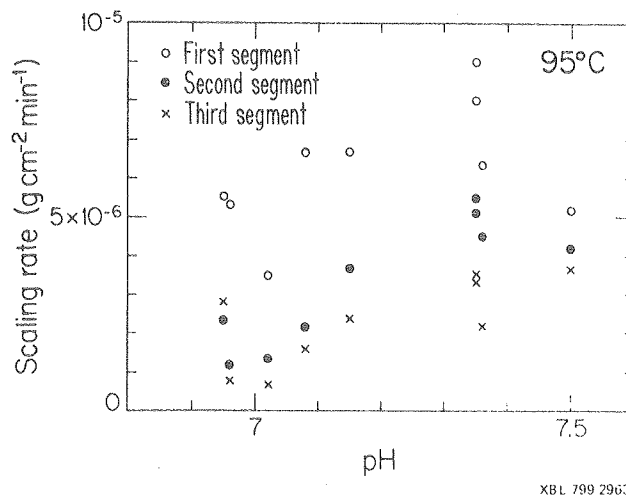


Figure 10. Effect of pH on scaling rate.

CONCLUSIONS

We have demonstrated that the chemistry of silica in Cerro Prieto brine may profitably be studied in the laboratory using synthetic brines. Because some properties of the brine vary greatly with its composition, such results must be confirmed in the field using actual brines. However, the results of the synthetic brine work are good enough to allow practical brine treatment processes to be proposed, and to contribute to the planning of a well-defined program of pilot-plant studies.

The same techniques could be applied to the study of silica chemistry in other silica-rich geothermal brines that precipitate relatively pure amorphous silica. These include the brines at Wairakei and Broadlands (New Zealand), Los Azufres (Mexico), and Baca site (USA).

The detailed conclusions and recommendations in this report are specific to Cerro Prieto. Experience has shown that even the variation between individual wells in one field can be great enough to make a treatment that works with brine from one well not work with that from another. The differences among fields are so large that, for all practical purposes, the problems at each field must be addressed separately. Of course, this is not to say that the experience gained and methodology developed in one place cannot be transferred to another.

Studying the precipitation of calcium carbonate from synthetic brines would be a trickier experimental challenge because of the volatile nature of carbon dioxide and because heterogeneous nucleation is probably important in the case of carbonates. However, properly designed and carefully executed experiments with synthetic brines should be able to address this problem as well. The same consideration applies to the other carbonates and sulfates.

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