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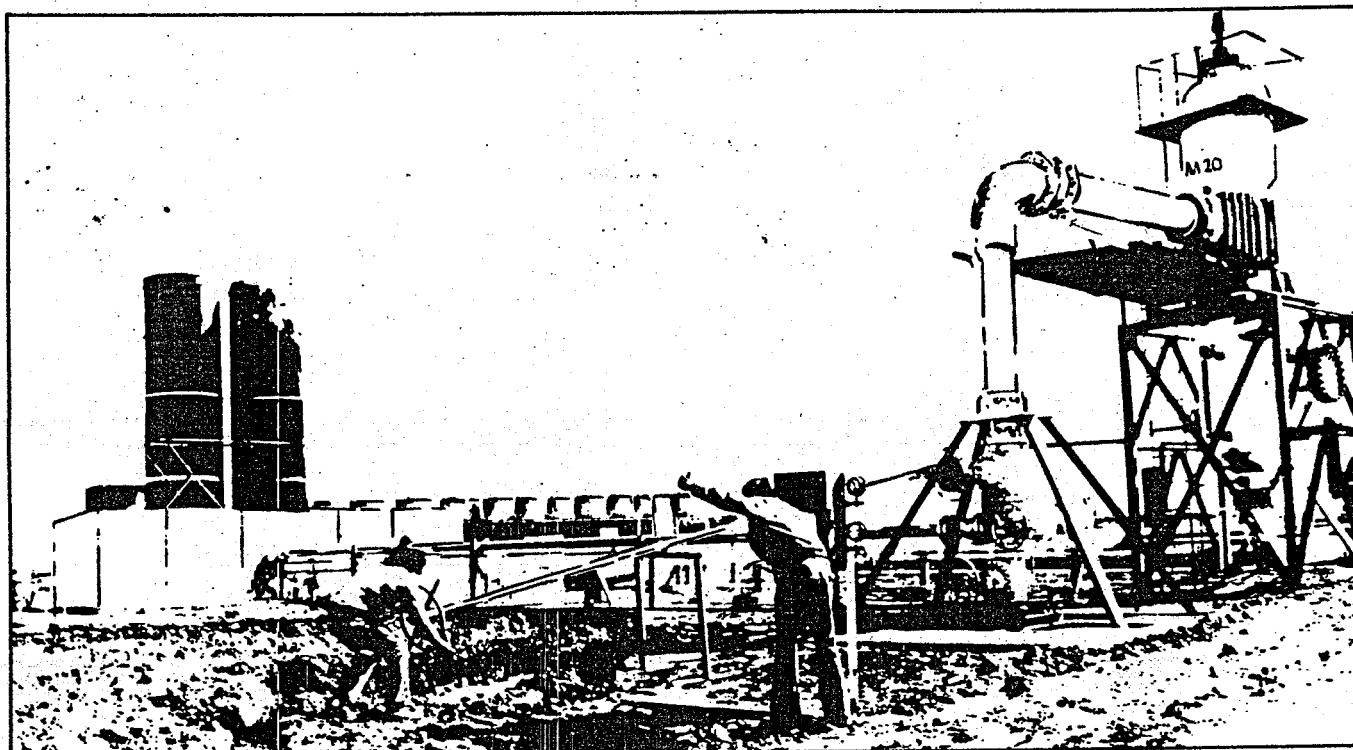
CHEMISTRY OF SILICA IN CERRO PRIETO BRINES

Oleh Weres
Leon Tsao
Eduardo Iglesias

April 1980

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CHEMISTRY OF SILICA IN CERRO PRIETO BRINES

by

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April 1980

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Abstract

The precipitation of amorphous silica from synthetic geothermal brines which resemble the flashed brine at Cerro Prieto has been studied. It was 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. Both in the laboratory and in the field quaternary amines were found 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 10-20 minutes in a covered holding tank, add 20-30 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.

The rate of deposition of silica scale from synthetic brines was separately studied. It was found that a modest decrease in pH could significantly reduce the scaling rate at a reasonable cost.

The equilibrium chemistry of Cerro Prieto brine was studied theoretically. These calculations indicate that increasing the brine pH to remove silica might cause some precipitation of carbonate minerals, but also that this problem could easily be eliminated at a reasonable cost if it did arise.

S1   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 Investigaciones Electricas (IIE). It was part of the research project at the Lawrence Berkeley Laboratory (LBL) which is part of the CFE-DOE Cooperative Program at Cerro Prieto.

For the purposes of this study, it was assumed that the brine to be reinjected will be flashed and separated from steam twice, and that it will 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 which form throughout the existing surface brine disposal system at Cerro Prieto.

Injecting brine which contains 400-500 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 means of controlling it.

Most of our work was experimental, and was performed in our laboratory using synthetic brines. Some field work was performed also at Cerro Prieto to verify the results obtained in our laboratory. The experimental techniques employed by us in this work are based on and 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., 1980).

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 recommended to them by us (see Section 7) 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 possiblity was studied theoretically.

Additional experimental techniques that were developed but not perfected as well as preliminary data generated by them are presented and discussed in the Appendices.

Much of the material in this report is contained in two papers that were presented by O. Weres and L. Tsao, and E. Iglesias and O. Weres, respectively, at the Second Symposium on the Cerro Prieto Geothermal Field that was held in Mexicali, October 17-19, 1979. These papers will be published as part of the Proceedings of this Symposium and will also be submitted for publicaton in Geothermics.

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S2   Real Brines and Synthetic Brines

The precipitation of amorphous silica from Cerro Prieto brines was studied 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 pH's. 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.

TABLE 1. Natural and Synthetic Cerro Prieto Brines

| | Natural Brines[*] | | | | Synthetic Brines | | | |
| | Well 14 | | Well 30 | | High Ca | | Low Ca | |
	mg L^{-1}	mmole L^{-1}	mg L^{-1}	mmole L^{-1}	mg L^{-1}	mmole L^{-1}	mg L^{-1}	mmole 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	.13	1.3	.07				
Sulfate	11	.11	13	.14				
Carbonate+Bicarbonate	50	.82	35	.57				
As	1.5	.02	.47	.006				
Ba	10.7	.078	8.0	.058				
Cu	<.05	<.001	1	.02				
Fe	.8	.014	.5	.009				
Mn	.2	.004	2.6	.047				
Sr	17.6	.20	18.8	.21				
Zn	.01	.0002	.01	.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.

It 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 which we consider unlikely to directly affect the chemical behavior of the the silica in the brine under the conditions of greatest interest were left out of our synthetic brines.

The pH value 7.3 chosen 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, $Si(OH)_4$. (Henceforth, "monosilicic acid" will be abbreviated "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 Weres, et al., 1980, Section 3.15).

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.

S3   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 0.3 L was usually employed.

Throughout our work with simulated brines, all volumes were measured at room temperature. Therefore, when we say 0.3 L, 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 semiquantitative nature of most of the synthetic brine data, this is, for all practical purposes, the same as moles or grams per kg of water.

The sodium metasilicate stock solution contained about 2 g L^{-1} 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 $CaCl_2$ and 0.0066 M H_3BO_3. 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 $CaCl_2$, and 0.0081 M H_3BO_3.

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 mg 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 gL^{-1} at the stated temperature. To approximately convert these values to units of $g(kg\ H_2O)^{-1}$, 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 with mixed anionic/cationic ion exchange resins. The water coming out of our laboratory's "D. I. water" tap was already once doubly deionized; as a precaution, we sent it through our own column filled with mixed resin 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 ($(NH_4)_6\ Mo_7\ O_{24} \cdot 4H_2O$), 47.0 ml concentrated NH_4OH (28% NH_3) 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 1.5 M H_2SO_4, and 500 ml D.I. 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 D.I. 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 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 step 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 mg per liter of the "clarified" synthetic brine.

When implemented as described above, this technique is unable to determine suspended silica concentrations greater than about 32 mg L^{-1}, because higher concentrations cause the spectrometer 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 D.I. 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 fifty.

In cases in which the "brine treatment" was apparently successful, the "Final Suspended Silica" values were usually in the range 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.

S4 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, 1972; Iler, 1975b; Weres,
et al., 1980, 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 report 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 to drop to a nearly steady state value. Next, the brine
was briefly stirred, the floc was allowed to settle for two 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 experi-
mental design like the duration of settling, the size and shape of the

SUSPENDED SILICA VS. pH

95°C
0.33gL^{-1} Ca^{+2}

XBL 799-2957
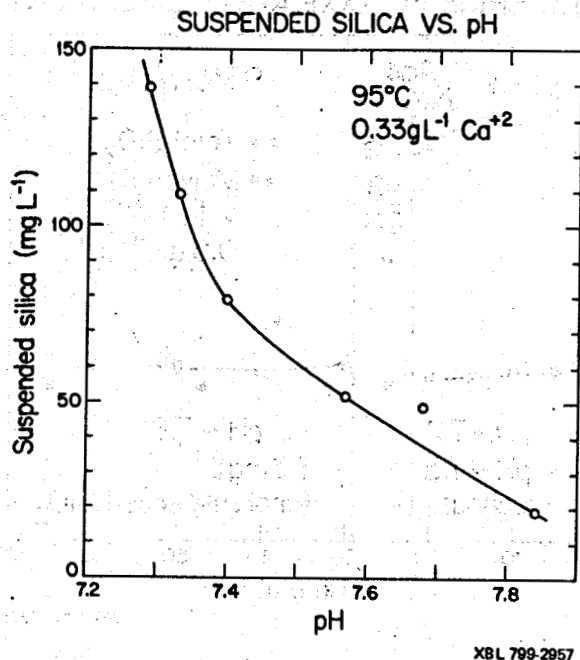
Fig. 1. The pH of this synthetic brine was progressively increased by adding NaOH, and the suspended silica determined after each increase.

reaction vessel, etc. However, it is obvious from Figure 1 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 is 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 that 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 polymeriza-

SYNTHETIC BRINE FLOCCULATION EXPERIMENTS
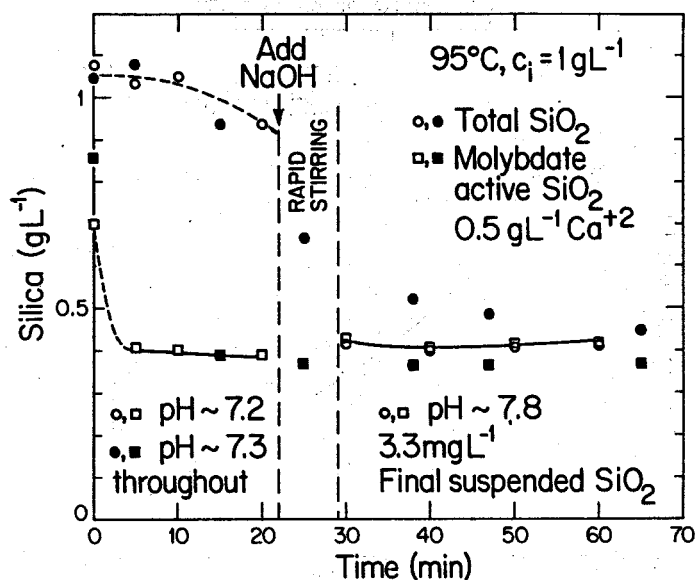
Fig. 2. Solid symbols: brine not "treated." Open symbols: pH increased after 22 min. by adding NaOH. In this and further similar Figures, silica concentrations not corrected for temperature effect. "High Ca" synthetic brine.

tion reaction had been completed by the time of the second point which was taken five minutes after the first. This means that a five-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. 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 g L^{-1}. (See Weres, et al., 1980, 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 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 to within experimental error. 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 g 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 re-equilibration 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 mg L^{-1} suspended SiO_2 was determined by the filtration technique. As discussed in Section 3, 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 g L^{-1}, which is still above of 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. (1980, Section 3.14), is about 5 micrometers $year^{-1}$. 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 mm sec^{-1}, and that its volume after having settled for about 100 sec is about 10 percent 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 g 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 Fig. 3 and Table 3.).

In one experiment 0.05 g 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 mg L^{-1} of calcium hydroxide would be needed to raise the pH to 7.8. (See Section 11.)

Rothbaum and Anderton (1975) have pilot tested a process for removing both suspended and dissolved silica from the brines at Wairakei and Broadlands 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 is 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.

SYNTHETIC BRINE FLOCCULATION EXPERIMENTS
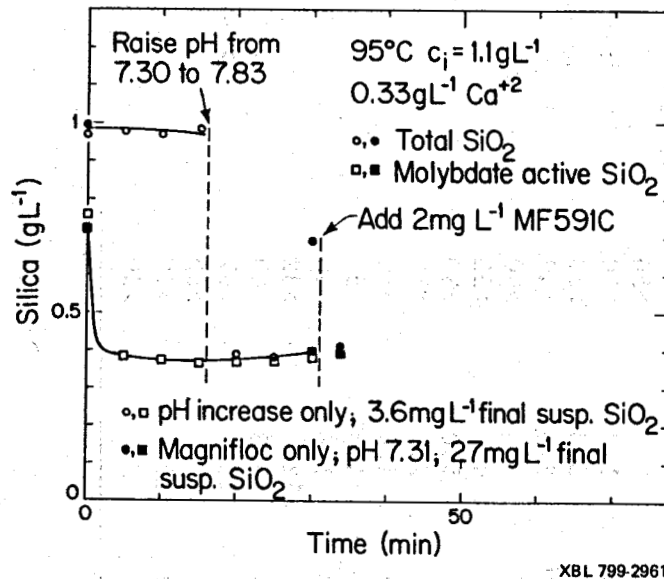
Fig. 3. "Low Ca" synthetic brine. Comparison of pH increase and addition of Magnifloc® 591C.

S5   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: $NR_4^+X^{-1}$). For a discussion of the general principles involved, see Iler (1973, pp. 53-63) and Iler (1979, pp. 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 two synthetic brine experiments with synthetic flocculants are presented in Figures 3 and 4.

The experiments in this series were like those discussed in Section 4, except that the requisite amount of the synthetic flocculant was added to the synthetic brine with stirring after about 30 minutes instead of 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

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 SiO_2	Final Suspended 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

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 SiO_2	Suspended 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

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.

TABLE 4

Synthetic Flocculants Tested

Manufacturer	Product	Chemical Nature
American Cyanamid	Magnifloc® 572C	Probably a monomeric quaternary ammine.*
"	" 573C	do.
"	" 577C	do.
"	" 585C	do.
"	" 587C	do.
"	" 591C	do.
"	" 1563C	Catonic polymer; otherwise unknown.
"	" 2535C	do.
Calgon	M503	Catonic 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.
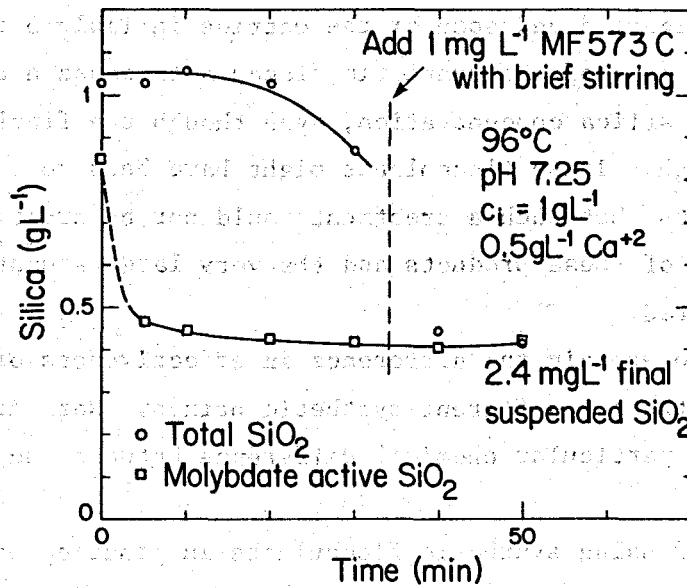
SYNTHETIC BRINE FLOCCULATION EXPERIMENT

Fig. 4. "High Ca" synthetic brine. Effect of Magnifloc® 573C.

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 mg L^{-1} in all cases, both with the High and Low Ca synthetic brines (Tables 2 and 3 and Figures 2 and 3).

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 and Figure 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. Figure 3 and 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, and

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, and

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, and

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 Section 11) or of an amorphous calcium silicate phase, and

2) the equipment used to produce lime milk or gel from quicklime is somewhat complicated and expensive.
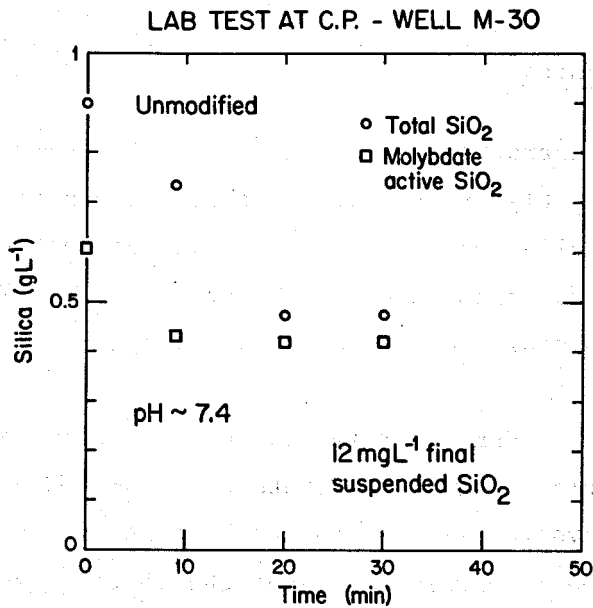
S6 Field Verification of Laboratory Results

A few experiments were performed at Cerro Prieto to confirm the laboratory results. These experiments were essentially the same as those discussed in Sections 3 to 5, 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.
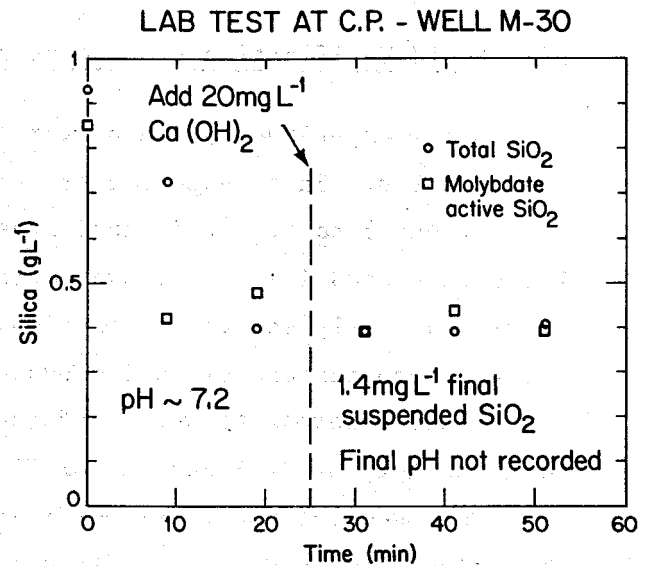
These experiments were performed at the CFE Laboratory at Cerro Prieto with the help of J. Fausto L. of CFE. Brine from Cerro Prieto wells M-14 and M-30 was used because these wells are conveniently near to the laboratory. The brine from M-30 is considered to be more representative of the field as a 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. This is illustrated in Figure 5, which presents the results of an experiment with M-30 brine that was not "treated." The amount of silica that remained in suspension after 30 minutes was low, but probably not low enough for reinjection. Figure 6 shows how well adding lime water to M-30 brine removes the suspended silica. Adding 2 mg L^{-1} of Magniflo©573C to M-30

LAB TEST AT C.P. - WELL M-30

XBL 799-2974

LAB TEST AT C.P. - WELL M-30

XBL 799-2975

Fig. 5. Experiment performed at Cerro
Prieto using freshly flashed brine
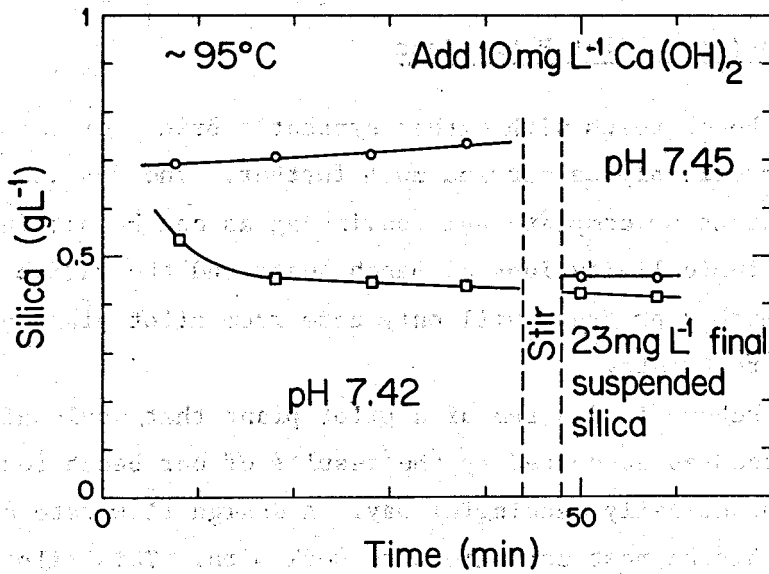from Well M-30. Brine not "treated".

Fig. 6.

brine 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 7 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 mg L^{-1}, would probably reduce the suspended silica in M-14 brine to
acceptable levels. The very small difference between the pre- and post-treat-
ment pH values in Figure 7 is probably due to experimental error.

Adding 2 mg L^{-1} of Magnifloc® 573C to M-14 brine did reduce the sus-
pended silica concentration to an acceptable level (Figure 8).

The volume and quality of the data we obtained in the field was reduced
by the difficulty of working in an unfamiliar laboratory, time constraints,
etc. 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.

LAB TEST AT C.P. - WELL M-14

~ 95°C   Add 10 mg L^{-1} Ca(OH)$_2$

pH 7.45

Stir

23mg L^{-1} final suspended silica

pH 7.42

XBL 799-2960

Fig. 7. One or both pH values may be in error.

LAB TEST AT C.P. - WELL M-14

Add 2mg L^{-1} MF 573C

○ Total SiO$_2$
□ Molybdate active SiO$_2$
pH ~ 7.4

2.7mg L^{-1} final suspended SiO$_2$
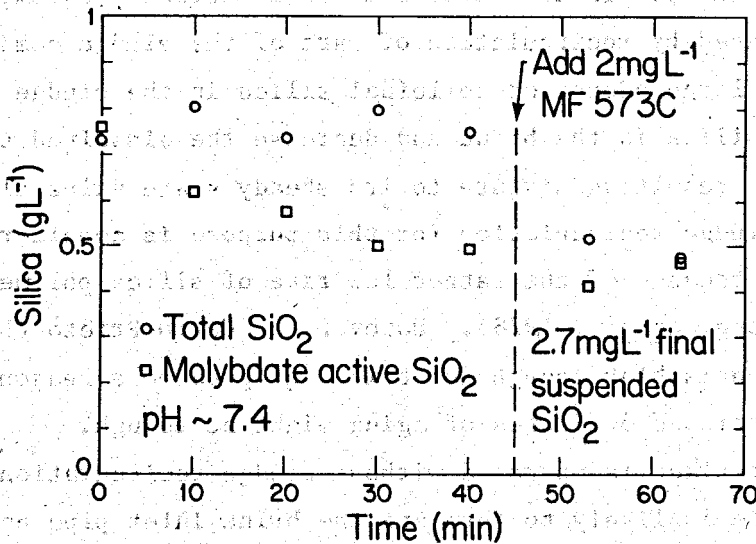
XBL 799-2977

Fig. 8. Effect of Magnifloc® 573C on brine from Cerro Prieto well M-14.

S7 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 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 9 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 m^3 hr^{-1} would probably be most convenient to work with. This pilot plant resembles the one used by Rothbaum and Anderton (1975).

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 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, the only places in which scale is likely to form are 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 doesn't come into contact with any part of the tank until a few minutes after it enters the tank and is already relatively nonreactive.

PROPOSED BRINE TREATMENT PILOT PLANT FOR CERRO PRIETO
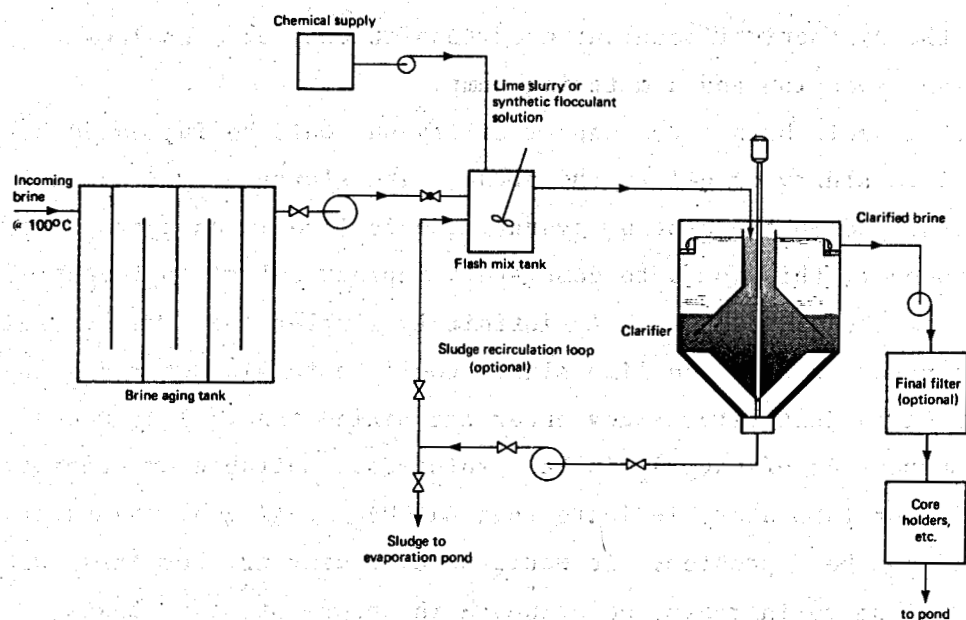
Fig. 9. Recommended brine treatment pilot plant facility for Cerro Prieto.

The sketch of the brine aging tank in Figure 9 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 9, 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 9 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 $Ca(OH)_2$ in NaCl solution. Suitable experiments performed in our laboratory indicate that $Ca(OH)_2$ 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 5-10 percent of the total volume of the incoming brine. Converting it to a concentrated sludge would compli- cate the process and equipment considerably. We recommend that it be simply disposed of by dumping it into the evaporation pond both in the pilot tests and in the ultimate commercial process . The existing evaporation pond at Cerro Prieto has more than enough capacity to handle the projected sludge output.

Drawing on related practical experience 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 to monitor the turbidity of the "clari- fied" brine. This instrument would allow suspended silica concentrations above about 10 mg 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. (See Section 3 and Appendix 2, respectively, for the techniques.) 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 continuously followed 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 petrographicallly 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 in Sections 8, 9 and 10.)

Both in the pilot plant and in the ultimate practical system, all equipment should be designed so as to keep air out of the system. Steam jacketing the major vessels is recommended for this prupose. Particular

efforts should be made to control heat loss from the small and complex "clari-
fied brine testing system" discussed above.

## S8   Scale Deposition from Synthetic Brines: Experimental Methods

Extensive solid and semisolid deposits of nearly pure colloidal amor-
phous 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 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 in Sections 3 to 5, and a continuous flow
kinetic system must be used.

The system developed for this experiment is schematized in Figure 10,
and several photographs of the apparatus are presented in Figure 11.   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 barbital in it is 2-1/2 times higher.
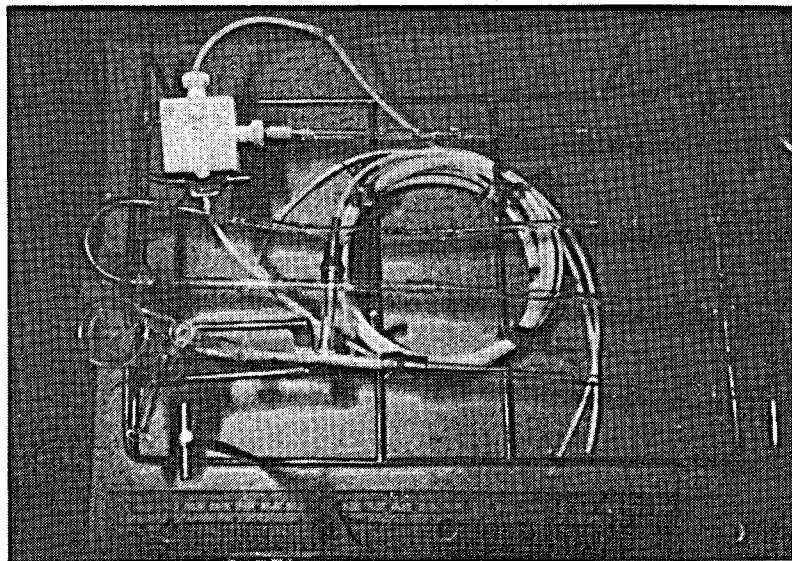
SYNTHETIC SCALE DEPOSITION APPARATUS
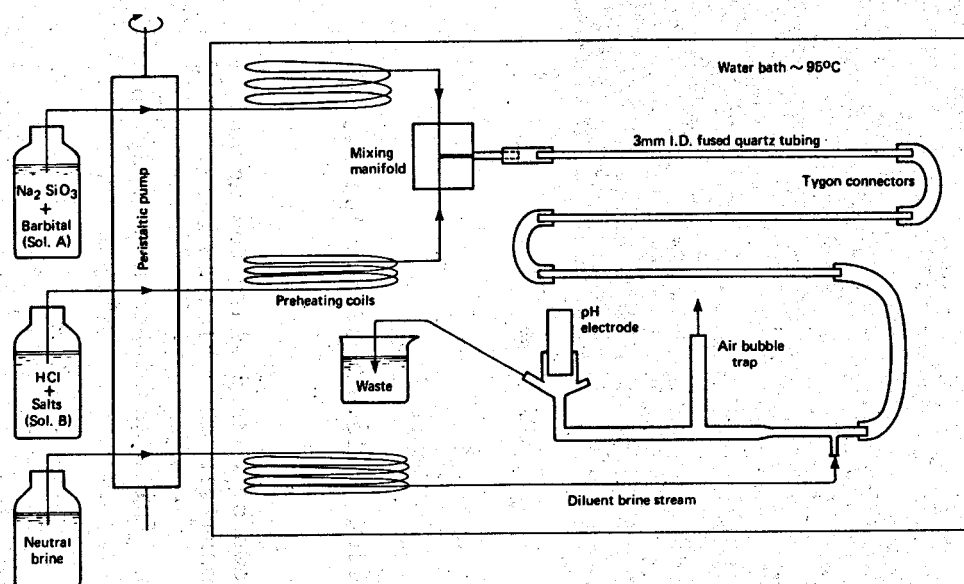
Fig. 10. There are actually four lengths of quartz glass tubing, and each of them consists of several short segments that are held together by Tygon® connectors. An early version of the "pH electrode manifold" is shown here.

The three solutions were pumped at equal rates by separate cassettes on a ten-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 meter 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 manageable proportions by 1) reducing the

(a)
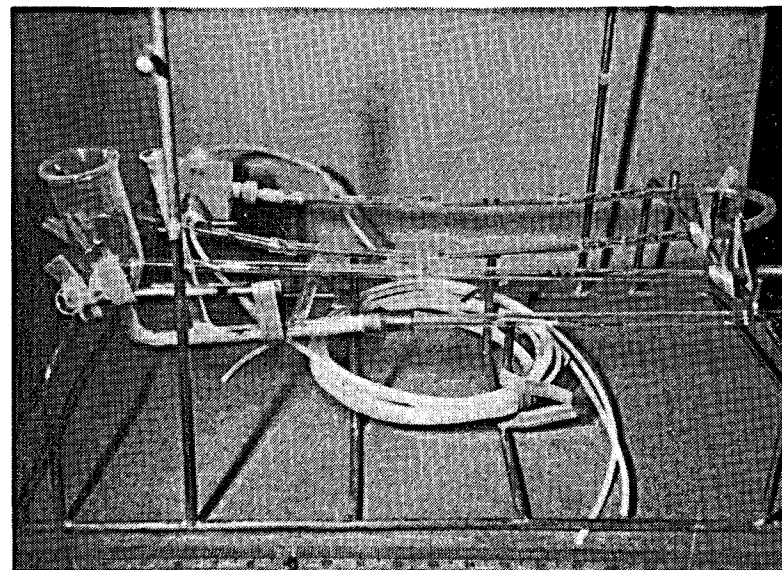
(b)
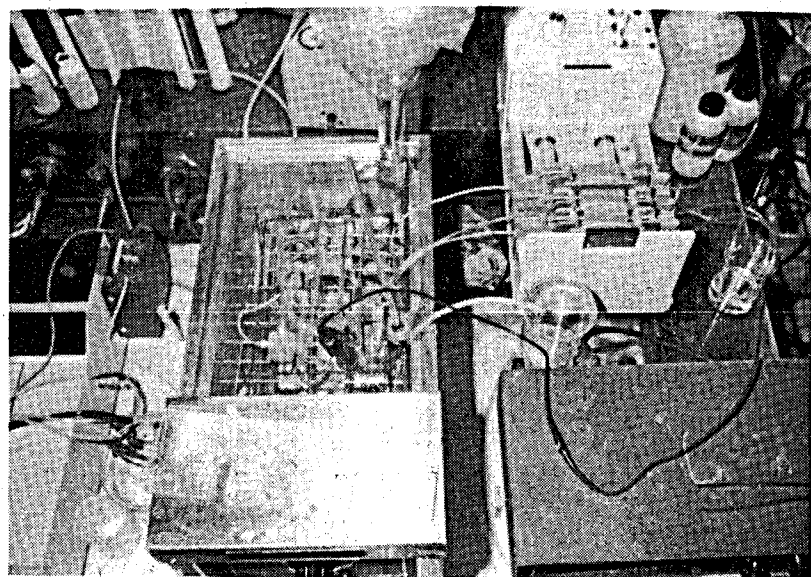
(c)

Figure 11

Synthetic Silica Scale Deposition Apparatus

(a), (b) Views of quartz glass tubing and
          pH manifold assembled on rack.

(c) Apparatus fully assembled and ready for
     startup.

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	2000	33.3			1000	16.7		0
Na From Na_2SiO_3	1530	66.6						
From NaBarb.	2299	100						
From NaCl			9389	498.4				
Total Na	3829	166.6			6610	288	6610	288
K			2872	74	1436	37	1436	37
Ca			1002	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			21655	610.8	10827	305.4	12409	350

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 ten 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 D.I. water and dried. Then they were "coded" with indelible ink for identification, and carefully weighed with an electronic balance to $\pm$ 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 10 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 ml 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 air bubbles
from the brine before it reached the electrode. This was necessary, because
air bubbles inevitably formed in the solutions during preheating, and caused
wild fluctuations in the pH reading if allowed to reach the electrode compart-
ment. 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 estab-
lished 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" of Sections 3 to 5, 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 ml 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 and the difference in weight before and after the reaction was the amount of silica deposited. This 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 10-15% 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.

Finally, some of the tube segments were scored lengthwise with a diamond scribe on both sides and then carefully broken. This procedure usually resulted in a few pieces suitable for microscopic examination and a small pile of crushed quartz glass.
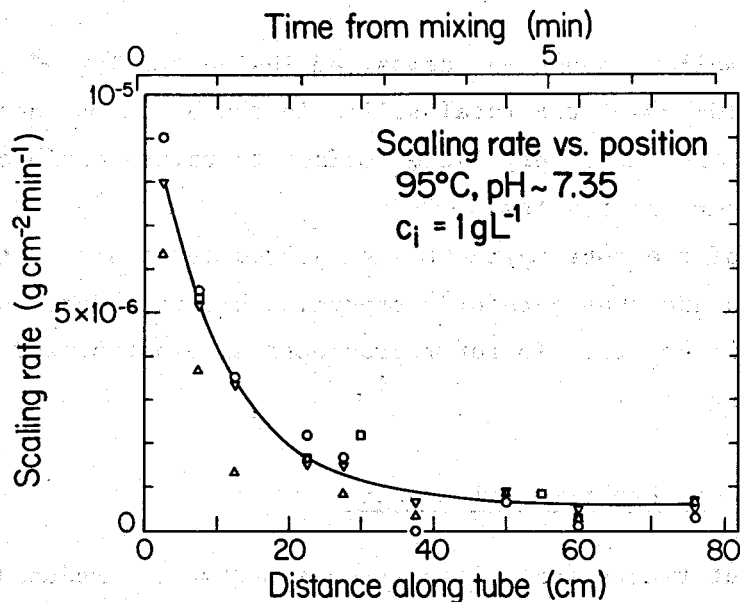
S9   Scale Deposition: Experimental Results

A total of about twenty 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 12. 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 that of the distance scale to account for the seven 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. However, it is easy to determine that the rate of scale deposition is one or two orders of magnitude greater than the rate of

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*See footnote on following page.

Fig. 12. Experimentally determined scale deposition rates as a function of position along the quartz glass tube and the time from mixing.

molecular deposition of dissolved silica under similar conditions.[*] This conclusively 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 to the curves of MAS <u>vs</u>. time presented in Figures 2, 3 and 4 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.

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[*] By "molecular deposition" we mean the deposition of dissolved silica onto a solid surface one molecule at a time. See Weres, <u>et al</u>. (1980) regarding the nature and kinetics of this process.
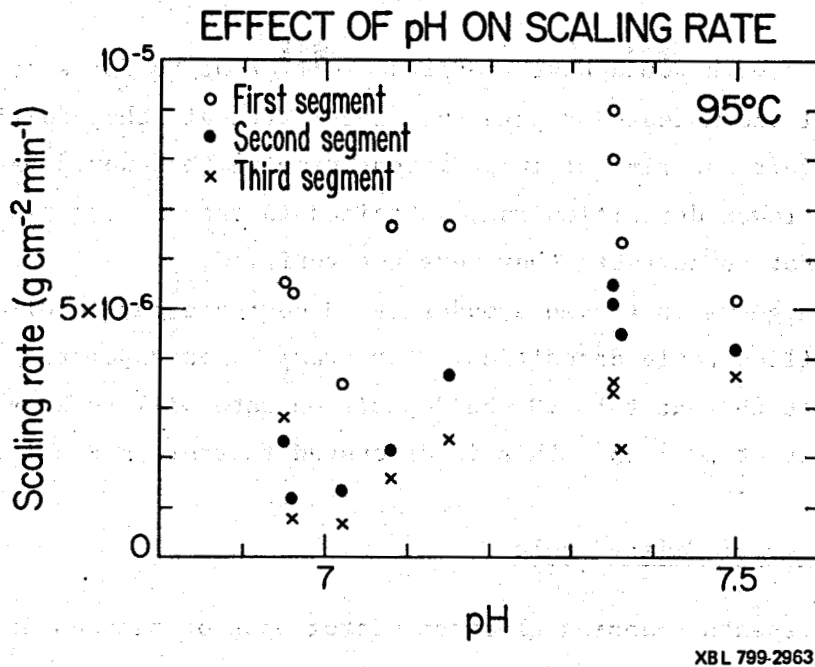
Fig. 13.

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 of the scaling process was originally proposed by Iler (1973, 1975 a).

Practically speaking, Figure 12 shows that aging newly flashed brine for three to five minutes should suffice to greatly reduce the scaling rate further along in the system.

Figure 13 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., 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 13 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 in Section 11.

S10 The Morphology of Silica Scale

Figure 14 presents scanning electron micrographs of samples of silica
deposits obtained from R. Hurtado J. of the IIE laboratory at Cerro Prieto.
The samples were collected by IIE personnel during tests of low pressure steam
separators, and all came from inside the test units. All three specimens
are essentially pure SiO_2. (This was determined using the micrsocope's
energy dispersion spectroscopy attachment.)

Figure 14 (a) shows a soft and fluffy white powder. This is basically
dried flocculated colloidal silica. There is little if any chemical cementa-
tion between the particles. The finest detail visible in the photograph is
on the scale of about 100 nm, and this suggests that the ultimate particle
size is about this or smaller. This material most closely resembles the
flocculated silica produced in the silica removal experiments discussed in
Sections 3 to 5.

Figure 14 (b) shows the broken edge of "typical" solid silica scale.
As is commonly the case at Cerro Prieto and elsewhere, this specimen was
stratified, with the macroscopic appearance of the various layers ranging
from white and porous to nearly vitreous and dark grey. This material
consists of densely packed colloid silica particles that have been cemented
into a solid by molecular deposition of dissolved silica between them.

Figure 14 (c) shows a sample that has been so thoroughly cemented that
it is completely glasslike and retains no trace of its colloidal origin. We
know that it did not form by molecular deposition alone because that process is
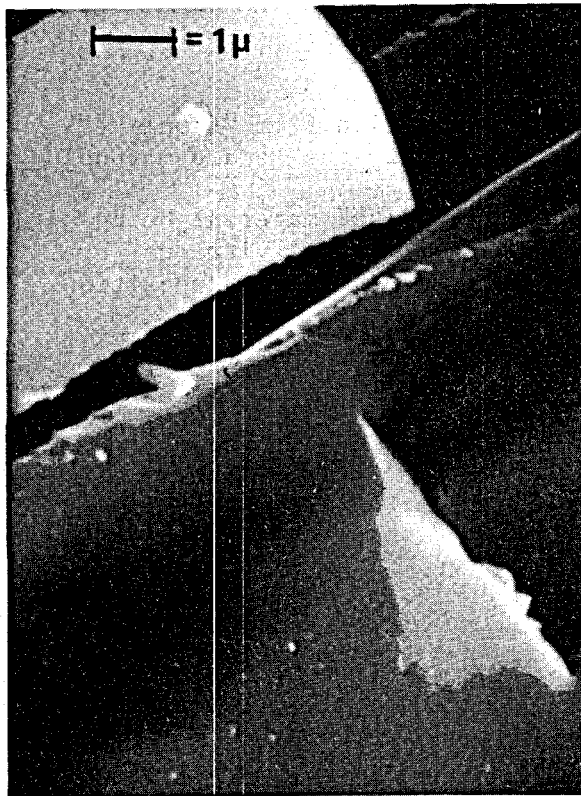too slow to form scale deposits in a short time under these conditions. Also,

Figure 14

Silica Deposits from Low Pressure Steam Separators
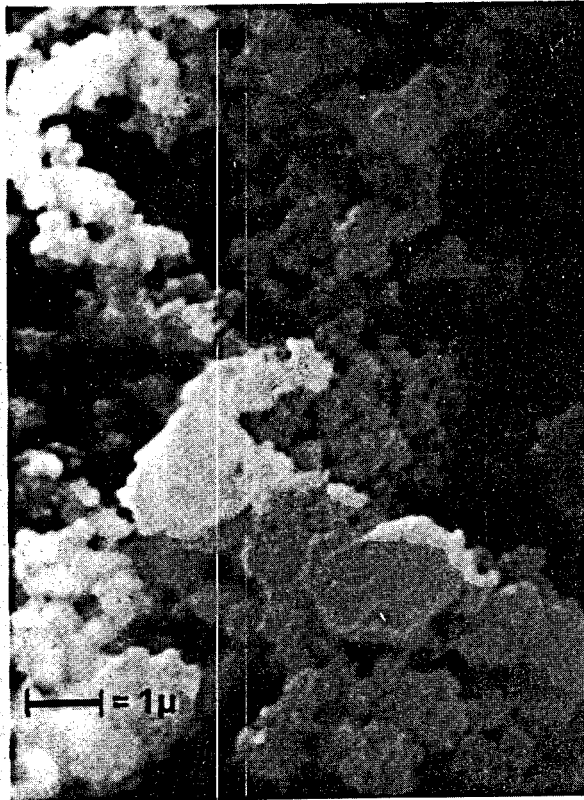
(a) XBB 801-688

(b) XBB 801-689

XBB 801-690

(c)
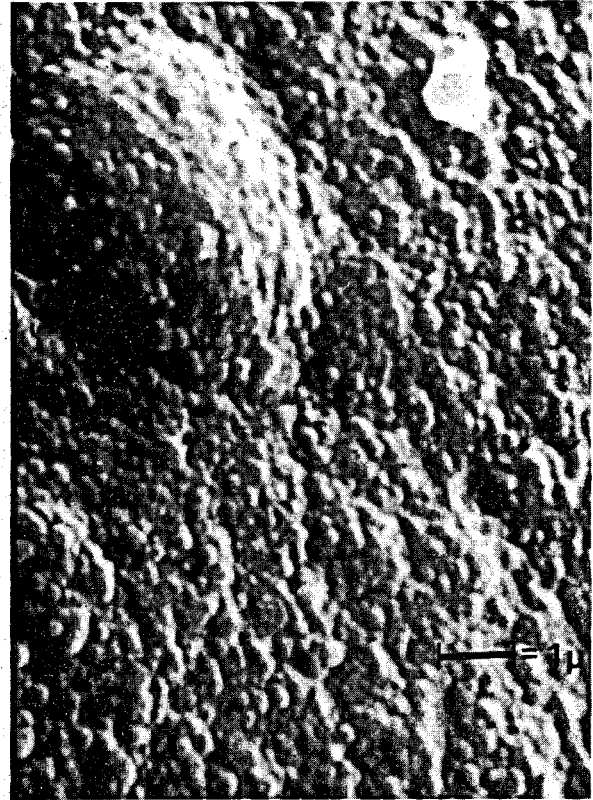
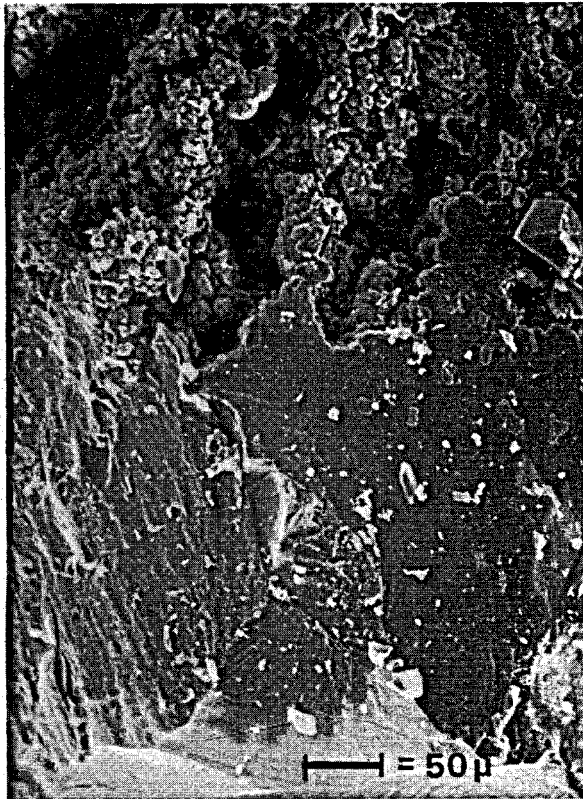(a) Light, porous white powder.

(b) Stratified, medium density, solid deposit; "typical" silica scale.
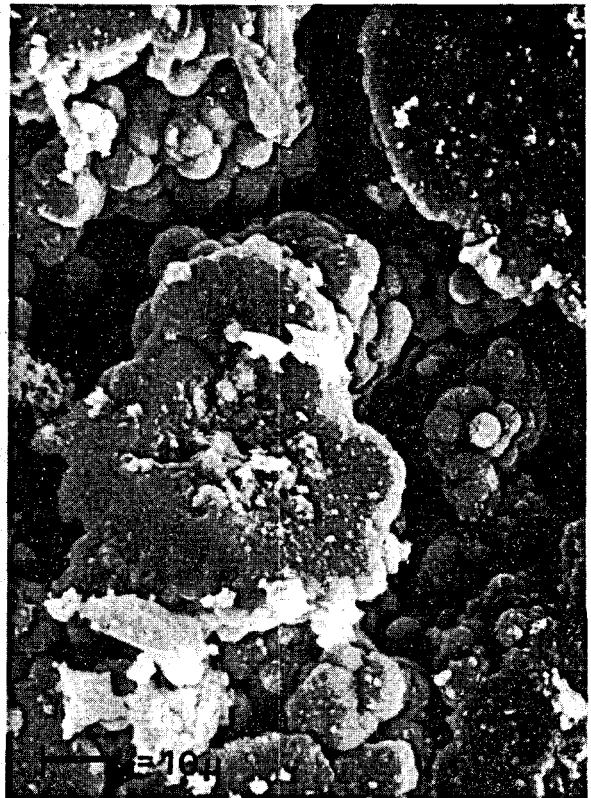
(c) Transluscent glass-like material.

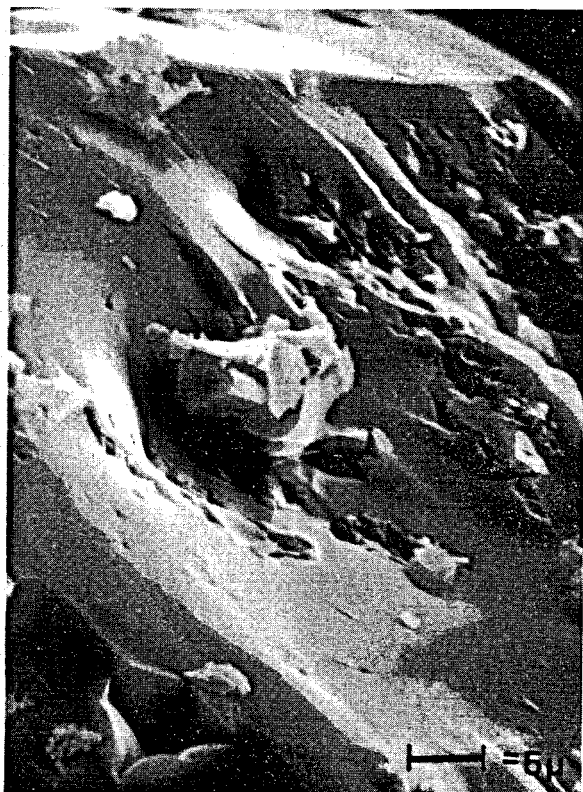All three photos are 10,000X scanning electron micrographs.

Figure 15

"Vitrified Scale" from a Low Pressure Brine Discharge Line

XBB 801-685

(a)

XBB 801-686

(b)

XBB 801-687

(c)

(a) Transition from "floclike"
     to "vitreous" scale morphology.

(b) "Floclike" material being
     converted to "vitreous" by
     dissolved silica deposition.

(c) "Vitreous" material with
     residual cavities.

on a macroscopic scale, this specimen shows obvious ripple-like "depositional structures" that could only have been formed by hydrodynamically controlled deposition of colloidal particles or clumps.

Figure 15 also illustrates the progression from floc-like to glass-like deposits. All three pictures are of the same specimen, but taken at different magnifications. Macroscopically, the sample is a light, porous, but locally vitreous looking inhomogeneous black material. It was collected from the brine discharge line of a low pressure steam separator, near the separator. The specimen consists mostly of SiO_2, but parts of it also contain significant concentrations of iron and other elements (determined by electron dispersion spectroscopy).

Figure 15 (a) shows both "floclike" and "vitreous" areas and the transition between them. Figure 15 (b) is a closeup of a "floclike" area which was gradually being "filled in" by molecular deposition of dissolved silica on what appears originally to have been a floclike material like that in Figure 14 (a). Figure 15 (c) shows a "vitreous" area which is glasslike except for some residual cavities.

Figure 16 shows typical "synthetic scale" samples produced in the experiments discussed in Sections 8 and 9. Figures 16 (b) and 16 (d) show the same specimen which was taken from the last (downstream) tube segment used in an experiment at pH 7.35. Figure 16 (a) shows scale deposited in the first (upstream) tube segment in the same experiment. Figure 16 (c) shows scale deposited in the first tube segment used in an experiment at pH 6.95. (Scale samples produced at different pH values may be compared because it was found that brine pH has little effect on scale morphology in the range studied.)

Figures 16 (a) and (b) show that, although the synthetic scale is solid, its microscopic structure resembles that of the powdery material shown in Figure 14 (a); i.e., the synthetic scale is only very weakly cemented. Apparently, longer times are required to form the well cemented structures shown in Figures 14 (b) and (c) and Figure 15. The two low magnification Figures 16 (c) and (d) show the grossly inhomogeneous macroscopic appearance of the synthetic scale. In the upstream segment shown in Figure 16 (c), the inhomogeneity takes the form of "patchy" covering of the tube wall. In the downstream segment shown in Figure 16 (d), much of the deposited silica actually
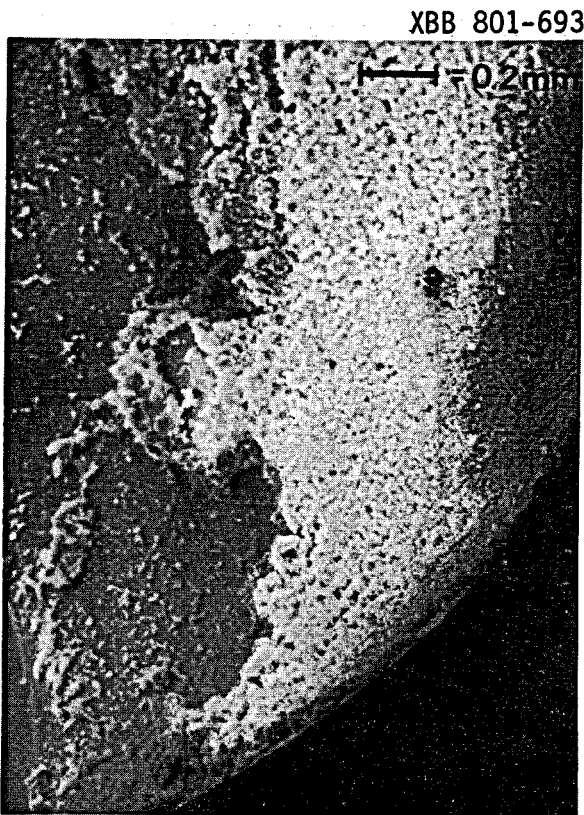
Figure 16

"Synthetic" Silica Scale
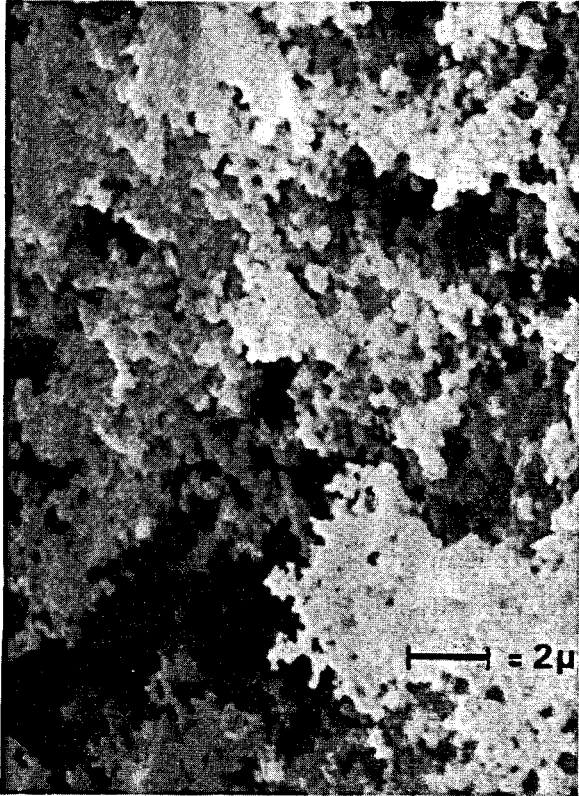
XBB 801-691
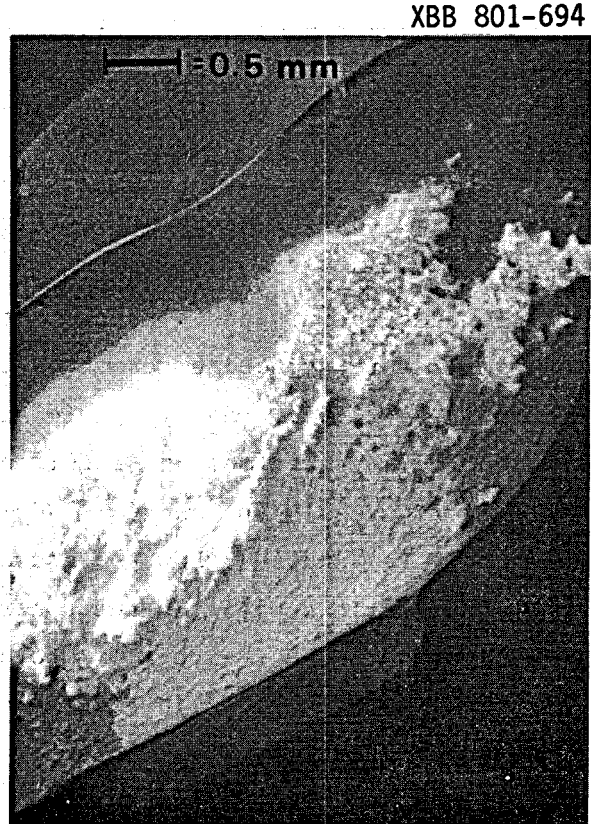
(a) Scale from first (upstream) tube segment, pH 7.35.
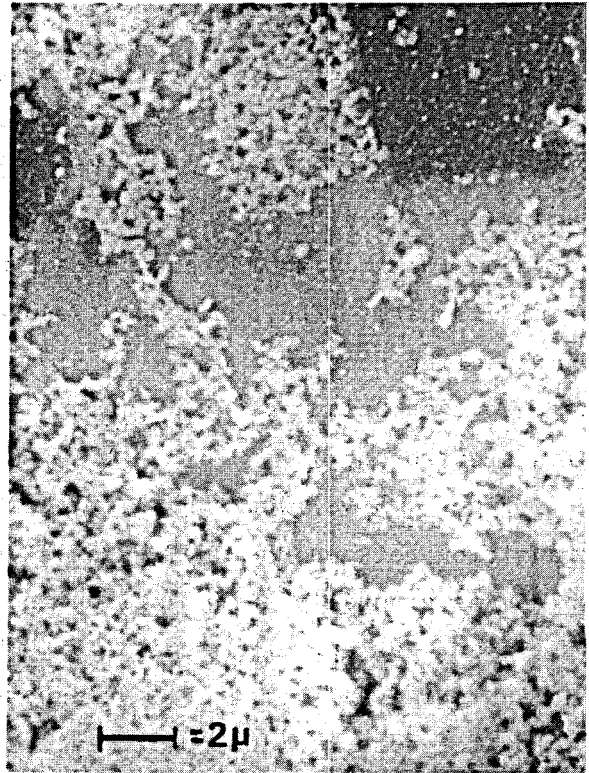
XBB 801-692

(b) Last (downstream) tube segment. Same experiment as (a).

XBB 801-693

XBB 801-694

(c) First tube segment, pH 6.95.

(d) Same specimen as (b).

settled on the bottom of the tube. (This is commonly visible to the naked eye
in the downstream tube segments.) The weaker cementation of the material in
Figure 16 (d) is demonstrated by the "glow" in the image, which is caused by
the inability of sputtered gold to render a very poorly consolidated specimen
conductive enough to prevent charge buildup. It is striking how little the
appearance of these specimens varies with magnification.

S11 The Equilibrium Chemistry of Cerro Prieto Brines

As was previously discussed, adding lime to increase brine pH appears
to be a promising method for removing suspended silica from the brine prior
to reinjection. However, increasing the pH carries the risk of causing the
precipitation of carbonate minerals. Using sulfuric acid to decrease the
brine pH to reduce silica scaling in the low pressure steam separators
carries the risk of inducing the precipitation of sulfate minerals.

To evaluate these possibilities we studied the acid-base chemistry of
Cerro Prieto brine and the solubility of carbonate and sulfate minerals in
it. We used a computer program that calculates the equilibrium chemical
properties of a brine of given chemical composition and enthalpy at a given
pressure. It resembles other such programs closely. It is called HITEQ, and
is an adaptation of another program that was originally developed by O. Weres
to model the chemistry of geothermal power plant condensate.

The basic assumption is that of full thermodynamic and chemical equi-
librium in and between the liquid and gas phases. (HITEQ does not model the
precipitation and dissolution of solid phases.) Depending on the enthalpy and
chemical composition of the system and the pressure specified, the system may
consist of a liquid phase only, a vapor phase only, or both. In a typical
two-phase situation the liquid phase contains dissolved gases as well as
non-volatile components, and the vapor phase is a mixture of steam and other
gases. The liquid-phase dissociation and complexing reactions, and the common
logarithms of their equilibrium constants, included in HITEQ are listed in
Table 6. The partition of gases between the liquid and vapor phases is
calculated using Henry's Law (Table 7). The mineral phases in SILNUC, and the
common logarithms of their solubility products at 100°C, are listed in Table 8.

Table 6

Solution Phase Equilibria in HITEQ

Reaction	log K(100°C)
$NH_3 + H_2O = NH_4^+ + OH^-$	-4.868
$H_2S = HS^- + H^+$	-6.624
$H_4SiO_4 = H_3SiO_4^- + H^+$	-9.097
$H_3BO_3 = H_2BO_3^- + H^+$	-8.950
$H_2O = OH^- + H^+$	-12.257
$CO_2 + H_2O = HCO_3^- + H^+$	-6.454
$HCO_3^- = CO_3^{2-} + H^+$	-10.159
$HCO_3^- + Na^+ = NaHCO_3$	-0.250
$HCO_3^- + Ca^{2+} = CaHCO_3^+$	1.450
$HCO_3^- + Mg^{2+} = MgHCO_3^+$	1.253
$HCO_3^- + Ba^{2+} = BaHCO_3^+$	2.268
$HCO_3^- + Sr^{2+} = SrHCO_3^+$	2.414
$CO_3^{2-} + Na^+ = NaCO_3^-$	1.209
$CO_3^{2-} + Ca^{2+} = CaCO_3$	3.716
$CO_3^{2-} + Mg^{2+} = MgCO_3$	3.460
$CO_3^{2-} + Ba^{2+} = BaCO_3$	2.851
$CO_3^{2-} + Sr^{2+} = SrCO_3$	3.257
$SO_4^{2-} + Na^+ = NaSO_4^-$	0.926
$SO_4^{2-} + K^+ = KSO_4^-$	1.261
$SO_4^{2-} + Ca^{2+} = CaSO_4$	2.666
$SO_4^{2-} + Mg^{2+} = MgSO_4$	3.089
$SO_4^{2-} + Ba^{2+} = BaSO_4$	2.216
$SO_4^{2-} + Sr^{2+} = SrSO_4$	2.509

H_2SO_4, HCl, NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, etc., are assumed to be completely dissociated.

Table 7

Gas - Liquid Equilibria in HITEQ

	K_H^* at 100^OC
$CO_2(aq) = CO_2(g)$	95.8
$NH_3(aq) = NH_3(g)$	0.276
$H_2S(aq) = H_2S(g)$	27.5
$N_2(aq) = N_2(g)$	2279.
$O_2(aq) = O_2(g)$	1271.

* Henry's Law Constant in units of bars molal^{-1}.

Table 8

Mineral Phases in HITEQ

Mineral name	Chemical composition	log K_{sp} at 100^OC
Calcite	$CaCO_3$	-9.495
Aragonite	$CaCO_3$	-9.334
Strontianite	$SrCO_3$	-11.973
Witherite	$BaCO_3$	-12.845
Anhydrite	$CaSO_4$	-5.165
Gypsum	$CaSO_4 \cdot 2H_2O$	-5.106
Celestite	$SrSO_4$	-6.936
Barite	$BaSO_4$	-9.238

The partial pressure of steam in the vapor phase is taken to be the saturation pressure of water at the calculated temperature. (The thermodynamic properties of pure water are used in HITEQ. This is an approximation, but an acceptable one at the moderate salinity of Cerro Prieto brine.) Ion activity coefficients are calculated using a simple version of the extended Debye-Hückel Theory. The data base covers the range 0-300°C.

HITEQ's output includes: the temperature, the specific enthalpies and mass fractions of liquid and vapor, the partial pressures of steam and other gases in the vapor phase, the concentrations of the various gases, ions, and complexes in the liquid phase, pH, ionic strength, and the saturation ratios of the carbonates and sulfates of calcium, strontium, and barium.

HITEQ and the chemical model that is embodied in it will be described in detail elsewhere (Iglesias and Weres, report in preparation).

First we used HITEQ to compute the chemical equilibrium state of a representative Cerro Prieto brine (Table 9). (This brine corresponds to the "Low Ca" brine of Table 1.) The pH of the "unmodified" brine was taken to be 7.35.

Starting out with this "unmodified brine", we either increased the pH by adding lime ($Ca(OH)_2$) or decreased it by adding H_2SO_4. (In these calculations, the concentration of dissolved SiO_2 was assumed to have been reduced to 500 ppm by its conversion to colloidal silica.) The calculated saturation ratios for the six important minerals as a function of pH are presented in Figure 17. (The saturation ratios for aragonite and gypsum are not shown here or in the following Figures, because they always lie just below the saturation ratios for calcite and anhydrite, respectively.)

The results in Figure 17 indicate that the "unmodified" brine is already supersaturated relative to the three carbonate minerals. However, carbonate precipitation from the flashed brine at Cerro Prieto has not been reported. Either the precipitation of the carbonate minerals is hindered by kinetic factors, etc., or the theoretical predictions of HITEQ are incorrect for some reason. This discrepancy between theory and empirical observation should be cleared up. In the meantime, these theoretically calculated mineral saturation ratios must be used with due caution.

TABLE 9

"Typical Cerro Prieto Brine" Composition

	ppm	molal
Na	6610.	.288
K	1436.	.037
Mg	1.2	.00005
Ca	328.	.008
Sr	15.8	.00018
Ba	11.3	.000082
B	11.	.001
Cl	11970.	.340
CO_2	44.	.001
$SO_4^=$	9.6	.0001
SiO_2	500 (1000)*	.008 (.016)
pH (100°C) 7.35		

* The total amount of SiO_2 initially present in the brine is about 1000 ppm. However, only that portion of it that is actually in solution (as opposed to colloidal silica in suspension) plays a role in the acid-base chemistry of the brine. The dissolved silica concentration rapidly drops to about 500 ppm after the brine has been flashed down to 1 bar and 100°C.

In any case, if the practical need were to arise, the high saturation ratios of the carbonates could be decreased by decreasing the concentrations of bicarbonate and carbonate in the brine. This could be accomplished by adding acid to the brine between the first and second stage steam separators (Figure 18). Adding acid shifts the HCO_3-CO_2 equilibrium toward CO_2 by decreasing the brine pH (Figure 19), and then the CO_2 is stripped out of the brine by the second steam separation process. (The first steam separator pressure assumed reflects current practice; see Alonso, et al.,1979.)

When the brine in Table 9 is "recombined" at 6 bars with the steam that it was separated from in the second flash stage, its temperature increases to 159°C and its pH decreases to 7.02. (In this calculation it is assumed that all of the SiO_2 remains in solution.) In this "unmodified" state the equilibrium ratios of the three forms of carbon dioxide are CO_2 : HCO_3^- : $CO_3^=$ :: 0.220 : 0.773 : 0.007. Figure 19 shows how the partition between HCO_3^- and CO_2 varies with pH when H_2SO_4 is then added. At pH = 5, CO_2 : HCO_3^- :: 0.961 : 0.039. The fraction of the total carbon dioxide present as CO_2 in this state is approximately the amount that would be stripped off by subsequent flashing. The amount of sulfuric acid required to lower the pH to this value is 0.6 millimoles per kg of brine (60 ppm). We do not anticipate that this moderate pH decrease would significantly increase corrosion problems. The calculated saturation ratios of the sulfate minerals as a function of pH when sulfuric acid is added at this temperature are presented in Figure 20. It appears that the solubility of barite may limit the use of inexpensive H_2SO_4 for this purpose.

Taking brine acidified to pH 5 with H_2SO_4 at 159°C and flashing it we find that the pH at 1 bar is 6.34 and that the total amount of carbon dioxide and bicarbonate remaining in the liquid phase is reduced to 3×10^{-3} mmole/kg. The effect of then adding lime to increase the brine pH upon the mineral saturation ratios is shown in Figure 21. We see that supersaturation with the carbonate minerals has been avoided. However, the brine is super-saturated with barite. This may be avoided by replacing all or part of the sulfuric acid with hydrochloric acid, but at increased chemical cost. The amount of $Ca(OH)_2$ needed to increase the pH of the separated brine to about 7.8, as required to flocculate the silica, was found to be about 0.5 mmole/kg, which corresponds to 28 ppm CaO. (In this part of the calculation the concentration of SiO_2 in the brine was again assumed to be 500 ppm.)
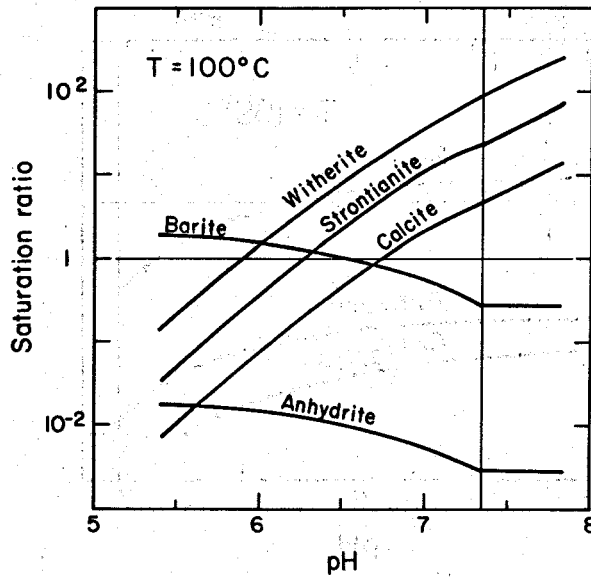

Saturation ratios at first separator
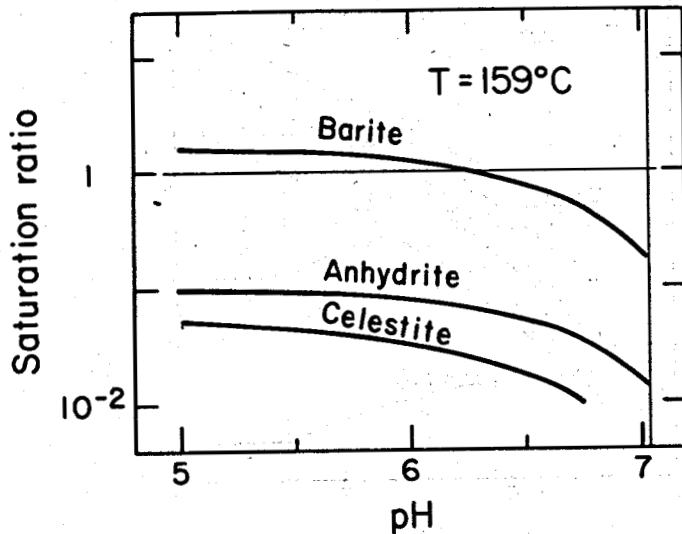
XBL 7912-13480

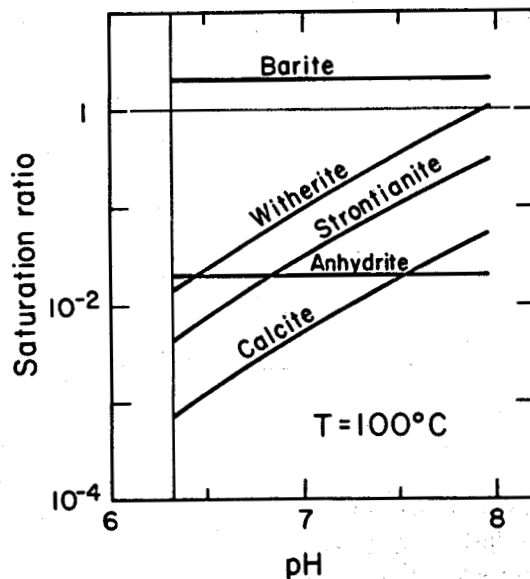Fig. 20. Effects of adding sulfuric acid on the saturation ratios of the
sulfate minerals.

Saturation ratios at second separator

XBL 7912-13482

Fig. 21. Effects of then adding lime to the flashed brine at atmospheric
pressure. Vertical line indicates the pH of the brine at 100°C after
its pH has been lowered to 5 at 159°C.

If both acid and lime are to be used, the lime should be added to the brine in two doses. First, enough lime should be added to the brine before it enters the aging tank to increase its pH to about 7.1. This would cause rapid polymerization, but would avoid premature flocculation in the aging tank. The rest of the lime needed to increase brine pH to about 7.8 would then be added to the mixing tank between the aging tank and the clarifier as before.

Assuming that 20 kg of separated brine is to be treated per kWh generated, we estimate that the amount of H_2SO_4 needed would cost about 2.0×10^{-5} US\$ kWh^{-1}; the cost of an equivalent amount of HCl would be 2.17×10^{-4} US\$ kWh^{-1}. The cost of the lime would be 2.0×10^{-5} US\$ kWh^{-1} in either case. These estimates are based on typical US West Coast bulk chemical prices quoted in the Chemical Marketing Reporter of January 21, 1980. The prices assumed were: US\$ 15 ton^{-1} for smelter grade 100% H_2SO_4 in tankcars; US\$ 62.50 ton^{-1} for 18° Baume HCl (29% by weight HCl) in tanks; and US\$ 32.50 ton^{-1} for quicklime (CaO) in pebble form, in 25-ton lots. These are prices "at the works." The cost of shipment to Cerro Prieto would increase them somewhat. (US tons assumed throughout this paragraph.)

These calculations suggest that the proposed scheme for preinjection brine treatment at Cerro Prieto is both technically and economically feasible. If increasing the pH does indeed cause precipitation of carbonates, this problem may be eliminated at reasonable cost by adding acid. Adding acid in the amount and place appropriate to this purpose would also reduce the rate of silica scaling in the low pressure steam separators and associated piping by fourfold or better (see Section 9 above).

These conclusions must, of course, be tested in the field by means of appropriate pilot scale experiments.

S12 Conclusions

It has been 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 based on them, 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
difference between different fields is 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.

Our limited effort to study the precipitation of calcium carbonate from
synthetic Cerro Prieto brine was unsuccessful. (See Appendix 2). This is 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 experi-
ments with synthetic brines should be able to address this problem as well.
The same consideration applies to the other carbonates and sulfates.

Our attempts to theoretically model the equilibrium chemistry of Cerro
Prieto brines produced mixed results. Our calculations indicate that unmodi-
fied flashed Cerro Prieto brine is supersaturated with calcite and other
carbonate minerals, but precipitation of carbonates in the wastewater system
at Cerro Prieto has not been reported. Overall, we feel that the only
immediately useful results to be expected from such calculations at this
time are theoretically calculated titration curves. These are indeed useful
for predicting the cost of modifying the pH of the brine. Calculated mineral
solubilities and saturation ratios can only be considered to express "the
potential for precipitation".

Aside from the usual problems of bad and/or incomplete data, we believe
that the uncertain quality of such theoretical predictions is in large
measure due to the inadequate and inconsistent theories of strong, mixed
electrolyte solutions now in common use. Each author uses his own version

of these theories to fit his experimental data or perform his calculations.
Because of this, the data in the various data bases is simply inconsistent.
The worst part of all this is the introduction of numerous "ion pairs", which
may or may not actually exist, into these models to compensate for the basic
inadequacy of the electrolyte theory employed. The values for the formation
constants of these "ion pairs" that are "determined" or "derived" or just
assigned by various authors sometimes differ by orders of magnitude. Pitzer's
(1973) powerful new theory appears to be a promising alternative to all
this. This theory is able to accurately fit the properties of strong elec-
tro lyte solutions with few parameters and without recourse to "ion pairs".

In this area of geothermal chemistry as in others, there is a great need
for careful comparison and reconciliation of theoretical predictions, labora-
tory data, and field observations.

Acknowledgements

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Appendix 1 Continuous Silica Recharge Experiment

It is of considerable practical interest to study the interaction
of dissolved silica with pre-existing flocculated colloidal silica, as in a
reactor clarifier. We developed an experimental method suitable for this
purpose and believe that it produces valid results. However, we did not have
the opportunity to properly verify these results or to work with the techni-
que enough to fully appreciate its possibilities and limitations.

It would not be practical to accumulate flocculated silica from a
large volume of flowing synthetic brine, as actually happens in a reactor-
clarifier. Instead, we prepared a small volume of synthetic brine in a
beaker and gradually added concentrated "silica recharge solution" to it
(using a peristaltic pump) without otherwise changing its composition.

The experiment was initially set up just like a silica removal experi-
ment of the kind discussed in Sections 3 to 5. The synthetic brine used was
formulated to resemble the High Ca synthetic brine of Table 1, except that
the barbital concentration in it was five times higher (0.1 M instead of
0.02 M).

A 0.2-L volume of this synthetic brine containing 1.0 g L^{-1} dissolved
SiO_2 was constituted in the usual way and its pH measured. It was then
allowed to sit undisturbed for ten minutes to let the dissolved silica
concentration drop to a nearly steady state value. Then "silica recharge"
was initiated by turning on the peristaltic pump. Two streams — one acid and
one basic — were continuously added to the brine from then on with rapid
stirring. The basic stream consisted of a sodium metasilicate solution that
contained 10.2 g L^{-1} dissolved SiO_2. The acid stream contained sufficient
HCl to neutralize the basic stream (0.34 M), the chlorides of sodium,
potassium, and calcium, and boric acid. The salt concentrations were double
those in the synthetic brine. The high concentration of barbital put into
the synthetic brine at the beginning was needed to keep the inevitable
slight mismatch between the two recharge streams from seriously perturbing
the pH.

The net effect of running the two recharge streams into the synthetic
brine was to add to the beaker a small amount of neutral brine whose salt
content was identical to that of the brine already in the beaker, but which

contained a much higher dissolved silica concentration and no barbital. In a mass balance sense, this is actually equivalent to what goes on in a reactor-clarifer. The only difference is that here much less water and salt are added, and no clarified brine "overflows."

At ten-minute intervals the pump was stopped, the time recorded, and the floc allowed to settle briefly. Then a sample of supernatant brine was drawn off with a 1.0-ml syringe for analysis, and the pH measured. Only MAS was analyzed for. After 100 minutes the experiment was ended and the final reaction volume recorded.

The specific rate of deposition of dissolved silica onto colloidal silica in g (g min)$^{-1}$ was determined from the data as follows:

First we calculated as functions of time

V = The volume of solution = $V_i + f_e t_r$

Q_t = total amount of silica present = $C_i V_i + C_r f_r t_r$

Q_d = total amount of dissolved silica = $CV = C(V_i + f_e t_r)$

Q_s = solid or colloidal silica = $Q_t - Q_d$

where

V_i = the initial volume = 200 ml

f_r = flow rate of each recharge stream = 0.5 ml min^{-1}

f_e = total "effective flow rate," corrected for evaporation losses

t_r = cumulative time duration of pumping

C_i = initial silica concentration in V_i.

C_r = concentration of silica in the basic recharge stream = 0.1692 M = 10.17 g L^{-1}

C = empirically determined MAS concentration

Although the total inflow rate was 1.0 ml min^{-1}, evaporation lead to a significant loss of volume. After 100 minutes the increase in volume should have been 100 ml, but the measured increase was 70 ml. It was assumed that the evaporation occurred at a constant rate. This gave an "effective flow rate" f_e of 0.7 ml min^{-1}, and this value was used to calculate Q_d.

V, Q_t, Q_d, and Q_s were calculated for each sample point.

Then

$dQ_s/dt = dQ_t/dt - dQ_d/dt = f_r C_r - dQ_d/dt$

R_s = the specific reaction rate = $Q_s^{-1} dQ_s/dt$

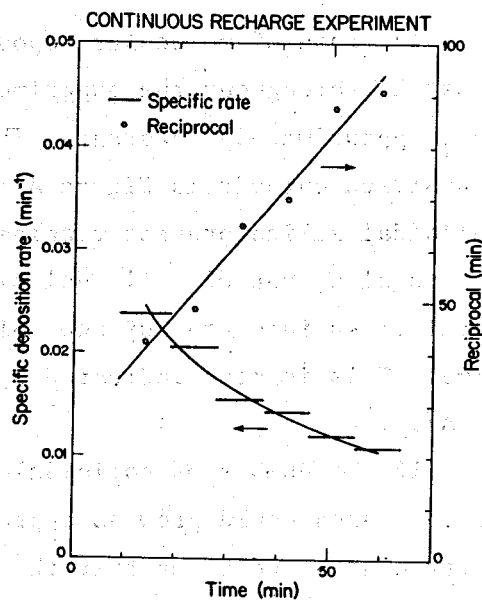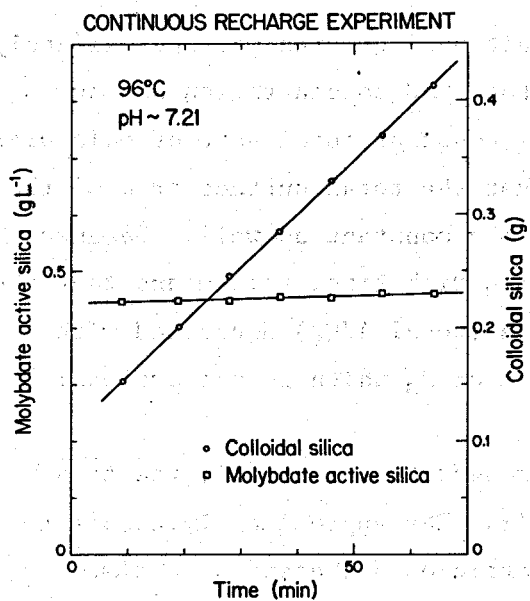In practice, since only a finite number of concentration measurements

Fig. A1. MAS concentration and total amount of colloidal silica present as a function of time from start of recharge.

Fig. A2. "Reciprocal" is that of the "Specific Deposition Rate".

were made, ratios of finite differences were used in place of derivatives:

$$\Delta Q_s/\Delta t = \Delta Q_t/\Delta t - \Delta Q_d/\Delta t = f_r C_r - \Delta(VC)/\Delta t$$

$$R_s = Q_s^{-1} \, \Delta Q_s/\Delta t$$

This calculation was performed for each interval between sample points.

The experimental and calculated results from an experiment of this sort are presented in Figure A1 and A2. The empirical values of C and calculated values of Q_s are presented in Figure A1. C remains essentially constant, and Q_s increases linearly with time. In other words, the "recharged" silica was converted to colloidal silica by molecular deposition on preexisting particles at a constant rate.

The calculated values of R_s and its reciprocal are presented in Figure A2. The values of R_s are plotted as horizontal bars rather than as points, consistent with the finite difference method used to calculate them. Each point represents a value of the reciprocal of R_s, and is plotted directly above the midpoint of the bar that represents the corresponding value of R_s. That these points "oscillate" about a straight line fitted to them is an artifact of the finite difference calculation.

The rate of molecular deposition per unit surface area was approximately constant throughout the experiment because both MAS concentration and pH were approximately constant. Therefore, the constant total rate of molecular deposition evident in Figure A1 indicates that the total surface area of the colloidal silica present remained approximately constant as well. Because the total amount of colloidal silica increased with time, this means that the specific surface area of the colloidal silica (total A/Q_S) decreased with time. This is also indicated by the decrease of R_S which is proportional to A/Q_S.

If the number of colloidal particles present were constant, the total surface area would grow as approximately $Q_S^{2/3}$. The approximately constant surface area indicates that the number of particles decreased with time. This decrease was probably due to the fusion of pairs of particles (see Weres et al., 1980, Section 3.12). No new particles were formed after silica recharge was initiated because the silica saturation ratio remained too low for homogeneous nucleation to occur.

Introducing the simplifying approximation that all of the particles are spherical and of about the same size, it is easy to show that the number of particles varies as Q_S^{-2} and that their average radius is proportional to Q_S. Also, the radius is proportional to $(A/Q_S)^{-1}$ and, therefore, to R_S^{-1}. Thus, R_S^{-1} should be proportional to Q_S. Comparing the plots of Q_S and R_S^{-1} in Figures A1 and A2, we see that this is true within the accuracy of the data; both Q_S and R_S^{-1} vary linearly with time, and both increase by about the same factor over 60 minutes.

The practical implication of all this is that sludge recirculation may be ineffective in reducing the dissolved silica concentration in Cerro Prieto brine. The reason is that recirculating the sludge does not appear to increase the surface area that is available for the molecular deposition of dissolved silica because the number of colloidal particles is continually being decreased by particle fusion. Of course, brine coming into the reactor-clarifier would introduce additional particles into the sludge. This does not happen in our experiment. However, these newly nucleated particles may be too small to continue growing at the relatively low dissolved silica concentration in the reactor-clarifier. Only more sophisticated laboratory experiments and/or field tests can resolve this question.

Appendix 2 Precipitation of Calcium Carbonate from Synthetic Brine

As noted in Section 11, freshly flashed Cerro Prieto brine appears to be supersaturated with calcite. This led us to attempt to study the simultaneous precipitation of calcium carbonate and amorphous silica from synthetic brine.

The synthetic brine used in these experiments differed from the High Ca brine in Table 1 only in that it contained 1 mmole L^{-1} of bicarbonate ion. This was put into the brine by adding the appropriate amount of sodium carbonate to the sodium metasilicate stock soluton. The additional amount of hydrochloric acid needed to convert the carbonate to bicarbonate was added into the acid, buffer, and salt mixture.

This synthetic brine was formulated in the usual way and its pH was increased after about 30 minutes by adding NaOH. The "clarified brine" was separated from the flocculated silica by decantation, and filtered to collect the solids that remained in suspension in it. Both the solids filtered out of the "clarified brine" and the flocculated silica were then analyzed for their calcium content. Only a trace of calcium was detected in either. This small amount probably came from the small amount of synthetic brine that remained with the solids.

This negative result may not have been meaningful. It is quite possible that much of the bicarbonate in the synthetic brine was lost by the escape of carbon dioxide during the experiment. (This would not have significantly changed the brine pH because of the presence of the buffer.) This problem could be eliminated by running the reaction in a sealed, completely liquid filled container, but we did not do this.

In any case, the following analytic procedure was employed:

The solids on the filter were washed into a 25-ml volumetric flask with enough 0.01 N HCl from a pipette to fill the flask. This solution was then analyzed for calcium using an atomic absorption spectrometer.

The flocculated silica was scraped and poured into two plastic centrifuge tubes and then spun down. This was repeated several times until all of the floc in the beaker had been transferred. The final volume of the spun down floc in each tube was about 4 ml.

The floc in one tube was washed three times by adding 8 ml of deionized

water and stirring, then centrifuging, and finally removing the water from above the precipitate using a pipette. Then the floc in each tube was extracted three times with 8 ml of 0.01 M HCl in a manner like the washing. The extract was placed in 50.0-ml volumetric flasks and made up to volume with deionized water.

The solution in each flask was then analyzed for both calcium and sodium by atomic absorption spectroscopy. Because the ratio of calcium to sodium in the brine is known, determining the sodium in the floc allowed us to approximately correct the amount of calcium measured by subtracting out the amount present in the brine entrained by the floc. Washing the floc removed most of the calcium and sodium that had been present in the brine entrained in it. Because there was apparently no solid calcium carbonate present in the floc, we were unable to determine whether or not this washing procedure would have dissolved away part of it.

We believe that these procedures are sensitive enough to detect less than 1 mg L^{-1} of solid calcium carbonate suspended in the "clarified brine," and less than 1% by dry weight of calcium carbonate in the floc.

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