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PRECIPITATION OF AMORPHOUS SILICA FROM HIGH-TEMPERATURE HYPERSALINE GEOTHERMAL BRINES

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MS. date: June 1975

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Abstract

A serious problem associated with the conversion of the energy content of hypersaline geothermal systems to electrical power is precipitation of amorphous silica and other phases that can ultimately cause scaling of power plant equipment. The rate of polymerization of monomeric silica is dependent upon pH, temperature, salinity, silica concentration, and the presence of solids. At the Salton Sea Geothermal Field, silica precipitation is promoted by cooling and depressurization. Evolution of CO_2 and H_2S causes an increase in residual brine pH, and, as a consequence, monomeric silica polymerizes more rapidly and is co-precipitated with sulfides and hydroxides. However, it may be possible to stabilize silica in geothermal brines by acidification with hydrochloric acid.

Introduction

The energy content of hot-water geothermal systems can be converted to electrical power by several processes. Total flow (Austin et al., 1973) denotes an energy-conversion system in which the entire wellhead product, water or a mixture of steam and water, is expanded directly to low pressure and low temperature to drive a turbine. The primary advantage of total flow, as compared to either a flashed-steam process, in which steam is separated from the fluid phase and used to drive a turbine, or a binary system, in which a heat exchanger is utilized to transfer energy from the geothermal brine to a working fluid, is its higher efficiency of energy conversion. However, one problem associated with all proposed systems for the utilization of hypersaline geothermal brines, similar to those which occur at the Salton Sea Geothermal Field (SSGF), is precipitation of silica and other phases that can ultimately cause scaling of plant equipment. The objective of this report is to discuss the aqueous chemistry of silica and then, using the SSGF as an example, to postulate a model that can account for its precipitation.

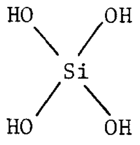
Aqueous Chemistry of Silica

A great deal of experimental data has been published concerning the solubilities of various forms of silica. Krauskopf (1956) compiled an excellent summary of the work completed prior to 1956. Since then, additional studies have confirmed the fact that both quartz and amorphous silica exhibit relatively high solubilities at elevated temperatures, pressures, and pH. The interested reader is referred to critical reviews of silica chemistry by Fournier (1970), Volosov et al. (1972), Wahl et al. (1974) and especially Iler (1955). To avoid confusion with terminology, Krauskopf's (1956) definitions of silica species, provided in Table 1, should be consulted.

Silica Solubility

Solubility data for various silica phases along the vapor pressure curve for water are summarized in Fig. 1. It is immediately evident that amorphous silica is more soluble than quartz at all temperatures. The data plotted in Fig. 1 were obtained for aqueous solutions at a pH of about 7. In saturated solutions with pH less than about 9, dissolved silica is in true molecular dispersion, and the primary aqueous species is the neutral monomeric molecule of orthosilicic acid, H_4SiO_4 (Alexander, 1953a; Alexander, 1953b; Alexander et al., 1954; Goto, 1956; Krauskopf, 1956; White et al., 1956; Okamoto et al., 1957; Fournier, 1970; Volosov et al., 1972). The primary species in superheated steam is also monomeric H_4SiO_4 (Morey and Hesselgesser, 1951; Kitahara, 1960a). Solubilities of all silica varieties increase at pH values that exceed 8.5 as a result of the dissociation of orthosilicic acid to the anions $H_4SiO_4^-$, and $H_2SiO_4^{-2}$ ($K_1 = 10^{-9.8}$; see Figs. 2 through 4).

Possible structures for aqueous silica species were reviewed by Iler (1955), Ingri (1959), Boehm (1966), and Snoeyink and Weber (1972). The structures are based on SiO_4 - tetrahedra. Monomeric molecules and ions are formed as follows:



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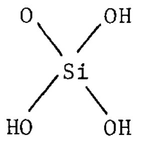

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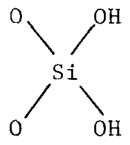


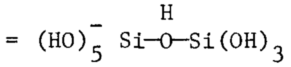
(-2)

According to Carman (1940), polymerization of monomeric species to particles of colloidal dimensions proceeds by the linking of adjacent SiO_4 - tetrahedra by Si - O - Si (siloxane) bonds:

$$-Si-OH + HO-Si = H_2O + -Si-O-Si-.$$

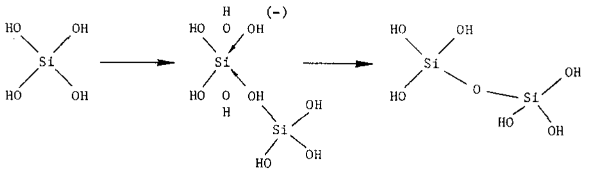
By analogy with SiF_6^{-2}, which is known to exist, Iler (1955) suggested that polymerization of silicic acid may involve a temporary increase in the coordination number of silicon from 4 to 6:

$$Si(OH)_4 + OH^- + Si(OH)_4$$



$$= (HO)_5^- Si\overset{H}{-O-}Si(OH)_3$$

$$= (HO)_3 Si O Si(OH)_3 + OH^- + H_2O$$



However, Ingri (1959) noted that, with the exception of SiF_6^{-2}, there is no other structural evidence for the existence of an $Si(OH)_6^{-2}$ ion.

Table 1. Crystalline, amorphous, and aqueous forms of silica (SiO_2).
(modified after Krauskopf, 1956)

Crystalline silica: Species of silica with crystal structure.

(a) *Macrocrystalline*.

Quartz, tridymite, or cristobalite.

(b) *Cryptocrystalline*.

Consists of fibrous crystallites with submicroscopic pores; general term is chalcedony.

Amorphous silica: Forms of silica lacking crystal structure.

(a) *Silica gel*.

Hard amorphous silica containing 20 to 30% water, prepared commercially either as a chemical reagent or as a desiccant.

(b) *Gelatinous silica*.

Appears in solution as gelatinous flocs or as a continuous gel, formed either by evaporation of a silica solution, by allowing a supersaturated solution to stand, or by acidifying a fairly concentrated solution of an alkali silicate.

(c) *Silica sol or colloidal silica*.

Silica dispersed in water in particles of colloidal dimensions (10^{-3} to 10^{-6} mm).

(d) *Opal*.

Naturally occurring silica, including the silica of diatomite and radiolarite, generally with less than 12% water. Some varieties appear to be transitional to crystalline material (cristobalite).

(e) *Silica glass*.

Prepared by the quenching of a silica melt.

Aqueous silica: Silica species in solution.

(a) *Orthosilicic acid*.

The principal form of silica in saturated solutions with pH less than 9 is the monomer H_4SiO_4. Above pH 9, orthosilicic acid dissociates ($K_1 = 10^{-9.8}$, Alexander *et al*., 1954).

(b) *Dissolved or colorimetric silica*.

The silica in true solution (H_4SiO_4) that reacts with ammonium molybdate within 2 min after the solutions are mixed.

(c) *Polymerized silica*.

Silicic acids containing two (disilicic), three (trisilicic) or more atoms of silicon per molecule (including colloidal suspensions). At room temperatures noncyclic silicic acids react with ammonium molybdate within 5 min, but cyclic polysilicic acids require several hours to react (O'Connor, 1961). High order polymers do not react at all. In unsaturated solutions, polysilicic acids depolymerize to the monomer (Alexander, 1954).

Table 1. (continued).

(d) Total silica.

All silica species in solution can be determined colorimetrically following conversion of polymerized silica to the monomer by treatment with NaOH, or by gravimetric techniques. In most natural waters gravimetric and colorimetric silica are identical, indicating the prevalence of the monomer H_4SiO_4.

Apparent colorimetric solubilities for silica in sea water must be multiplied by a factor of 1.23 (called the salt factor) to bring them into correspondence with solubilities in pure water (Chow and Robinson, 1953). The correction is probably the result of electrolyte interference with the colorimetric determination. Interferences can be minimized by maintaining a total ionic strength (with the exception of Mo) of less than 0.5 (Strickland, 1952).

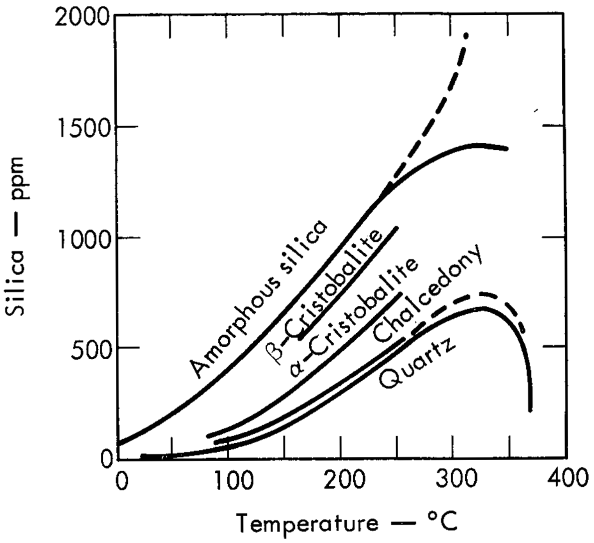


Fig. 1. Solubilities of various silica phases along two-phase curve (water plus vapor)(from Fournier, 1970).

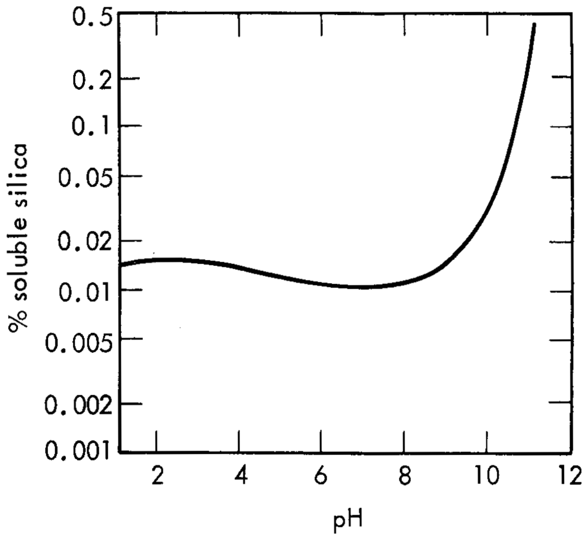


Fig. 2. Solubility of silica in water (25°C) (from Alexander *et al.*, 1954).

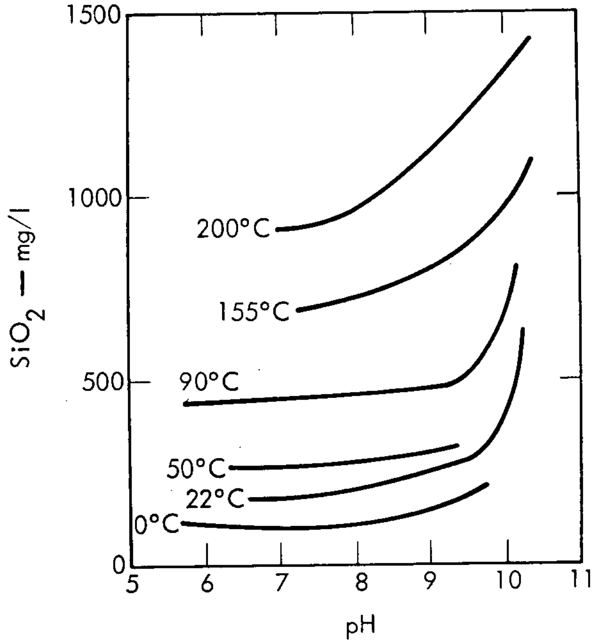
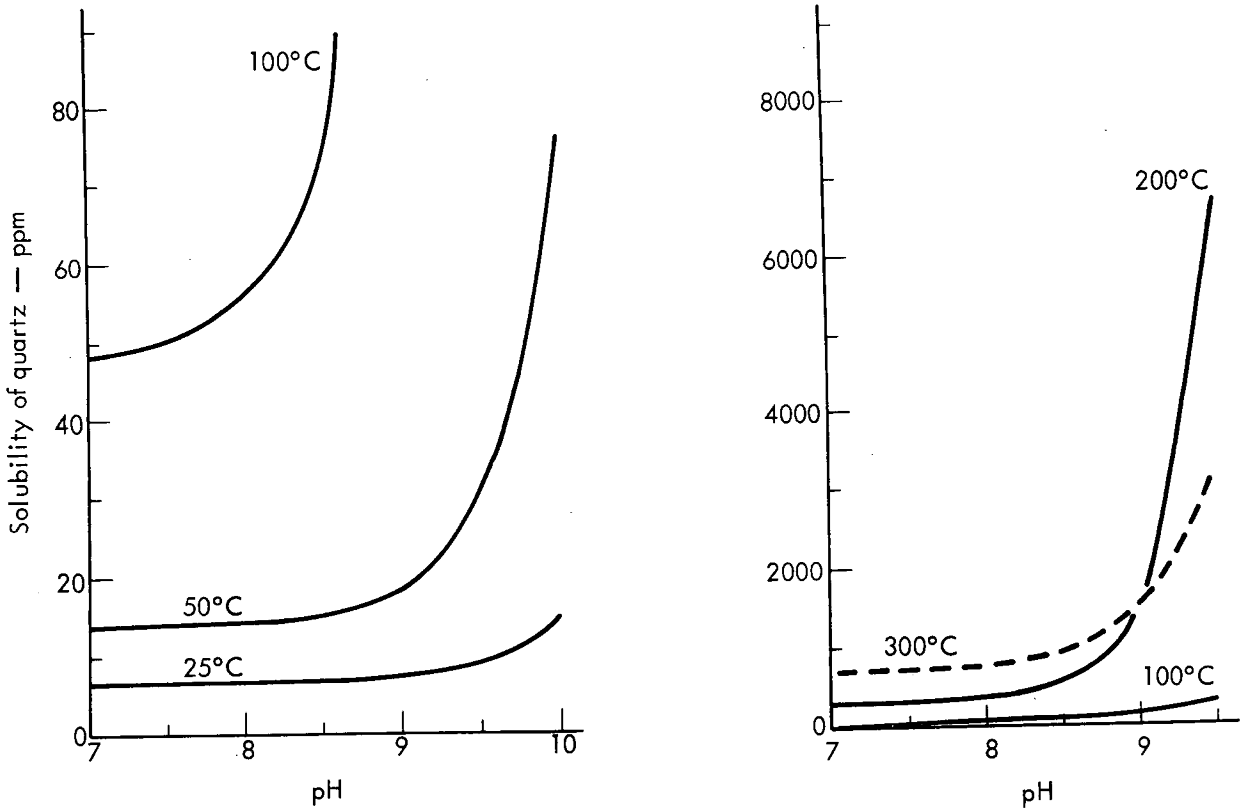


Fig. 3. Solubility of amorphous silica (from Okamoto *et al.*, 1957).



(a) Low temperature

(b) High temperature

Fig. 4. Calculated solubility of quartz (from Fournier, 1970).
(a) Low temperature.
(b) High temperature.

The steps involved in the polymerization of monomeric silica species to the ultimate precipitation or aggregation of particles of colloidal dimensions were summarized by Iler (1955):

$$\mathrm{Si(OH)_4} \xrightarrow{\text{Polymerization}} \text{Colloidal (sol)}$$

$$\text{particles} \xrightarrow{\text{Aggregation}} \text{Network of particles (gel)}$$

$$\text{Dilute sol} \xrightarrow{\text{Aggregation}} \text{Weak gel or}$$

precipitate

$$\text{Concentrated sol} \xrightarrow{\text{Aggregation}} \text{Strong firm gel}$$

$$\text{Wet gel} \xrightarrow{\text{Drying}} \text{Shrunken gel: Surface of}$$

particles in gel covered by Si OH groups.

A peculiarity of silica chemistry is the fact that when a solution becomes supersaturated with respect to amorphous silica, upon standing, or cooling, quartz does not crystallize. Instead, molecularly dissolved silica slowly polymerizes to a colloidal suspension that may ultimately precipitate as amorphous silica. Krauskopf (1956) emphasized this point. He noted that although quartz should theoretically crystallize from a solution saturated with respect to amorphous silica, it fails to do so, because of the slow reaction rate. Morey *et al*. (1964) also cautioned that the equilibrium between solid amorphous silica and dissolved silica is a metastable equilibrium because the stable form of solid SiO_2 at room temperature and pressure is α-quartz.

A second peculiarity of silica chemistry was pointed out by Hitchen (1935). He observed that silica is unable to accommodate itself rapidly to changing conditions, especially temperature decrease. As an example, Hitchen reported that it was possible to withdraw a high-temperature, neutral solution (310°C) containing 1800 ppm SiO_2 from a hydrothermal bomb by means of a steel condenser tube and to store the solution at room temperature for several months without precipitation of amorphous silica. He concluded that high-temperature saturated solutions showed no tendency to deposit silica (form scale) on the inner walls of the condenser tube! At room temperature, the silica remained in solution as a hydrosol.

Subsequent studies have demonstrated that the quenching of high-temperature saturated solutions of monomeric silica ($pH < 7$) does not result in immediate polymerization of dissolved silica (Okamoto *et al*., 1957; Krauskopf, 1956; White *et al*., 1956; Kitahara, 1960b; Morey *et al*., 1961; Morey *et al*., 1962; Fournier and Rowe, 1962). For example, White *et al*. (1956) and Morey *et al*. (1962) indicated that silica did not polymerize for several months after slightly acidic hot-spring waters, with 400 to 500 ppm dissolved silica, were cooled to room temperature.

In supersaturated solutions at low temperatures (less than 100°C), silica slowly polymerizes over a period of months (or years) until the concentration of dissolved silica is reduced to the equilibrium value. Rates of dissolution of solid silica phases are also low at low temperatures (Figs. 5 and 6). At high levels of supersaturation, silica sols may eventually precipitate as flocculent masses, in weakly basic solutions, or set to a gel, in weakly acidic solutions (Iler, 1955). Colloidal silica in undersaturated solutions depolymerizes until the equilibrium silica concentration, with respect to amorphous silica, is reached. The rate of depolymerization of colloidal silica is accelerated by the electrolytes in sea water (Krauskopf, 1956; Okamoto <u>et al</u>., 1957). Krauskopf (1956) emphasized that a true equilibrium solubility is established by depolymerization of colloidal suspensions. Hitchen (1945) postulated a peptization equilibrium of the type:

Solid phase > Molecular dispersion > Colloidal dispersion

to account for the solubility of silica in water. However, it should be emphasized that saturated solutions of silica, formed by dissolution of solid silica phases (or by the dissolution of polymeric molecules)

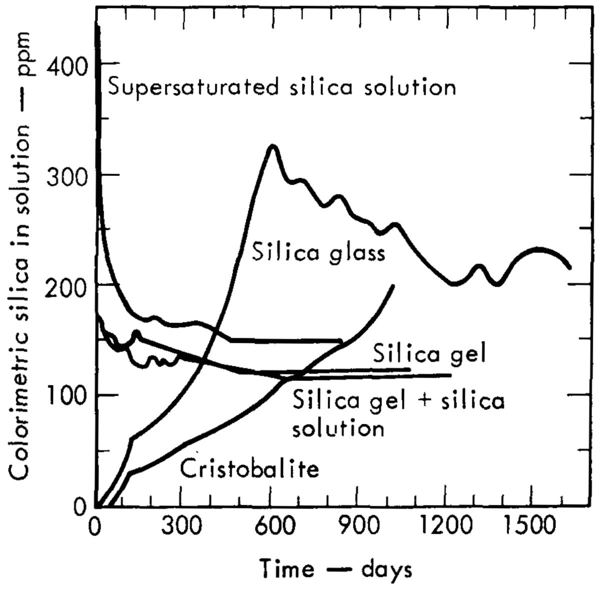
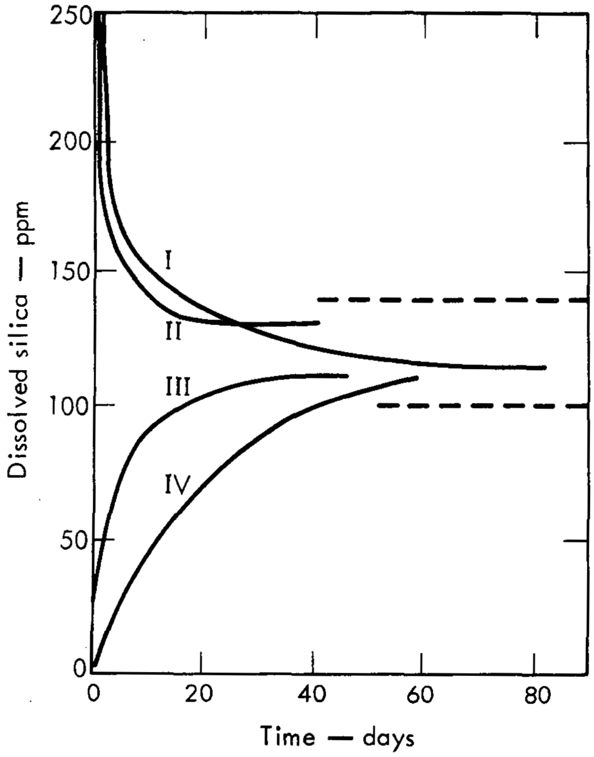


Fig. 5. Rates of solution and polymerization of amorphous silica in water at 25°C (samples were tumbled in water at 75 rpm, and silica in solution was measured at intervals by colorimetric molybdenum blue method)(from Morey et al., 1964).



Curve	pH	Initial total SiO_2 (ppm)	Initial dissolved SiO_2 (ppm)
I	7.7 - 8.3	320	284
II	7.3 - 7.9	975	544
III	8.3 - 7.4	187	25
IV	5.2 - 5.6	(silica gel in water)	

Dashed lines show the solubility range for 25°C, 100-140 ppm SiO_2, as given by Alexander, Heston, and Iler (1954).

Fig. 6. Approach to solubility equilibrium from both sides (from Krauskopf, 1956).

remain stable indefinitely although excess solid phases are removed from solution.

For example, in experiments designed to determine the solubility of silica in sea water, Krauskopf (1956) concluded that solubility was not affected by the electrolytes in solution. He noted that in initially supersaturated solutions, equilibrium concentrations of dissolved silica were relatively rapidly achieved ($pH > 7$). Excess silica was polymerized to colloidal suspensions and coagulated by the electrolytes in the solution. Once reached, the equilibrium concentration of dissolved silica remained constant even though colloidal silica precipitated.

Van Lier _et al_. (1960) found that quartz solubility is not affected by NaCl at salt concentrations below 10^{-1} _N_. At a NaCl concentration of 10^{-1} _N_ quartz solubility is slightly increased. However, dissolution rates are increased by concentrations of 10^{-2} _N_ NaCl, or higher (see also Kitahara 1960a). As an explanation for the observed NaCl effects, Van Lier _et al_. (1960) referred to previous work by Sadek (1952), which indicated complex formation between SiO_2 and HCl in a ratio of 1:1. The effect of sodium chloride on quartz solubility was also studied by Kitahara (1960c). He reported an increase in solubility, resulting from the greater density of brine solutions as compared to pure water, at temperatures higher than 300°C. However, Fournier and Rowe (1966) concluded that Kitahara's (1960c) high solubility results reflected contamination of his experimental apparatus with NaOH. Subsequent analyses by Fournier and Rowe indicated that the solubility of quartz is unaffected in 2M NaCl solutions.

Polymerization of Dissolved Silica

Factors that control rates of polymerization of dissolved silica from monomeric to polymeric molecules (including colloidal suspensions) are pH, salinity, degree of supersaturation, presence of solid substances, and temperature.

Colloidal particles of silica in alkaline solutions are negatively charged and, therefore, kept from coagulating by their mutual repulsion (Carman, 1940).

However, in the presence of soluble salts negatively charged particles are susceptible to neutralization by cations. At pH values between 1 - 3 colloidal silica particles pass through the isoelectric point (the point where their electrostatic charge is neutralized) and are, therefore, susceptible to rapid aggregation (Carman, 1940; Iler, 1955). In solutions more acidic than those with a pH of 3, colloidal silica particles become positively charged and are unaffected by other cations in solution (Iler, 1955).

The presence of $(OH)^-$ and $(F)^-$ ions catalyze the polymerization of colloidal silica (Iler, 1955; Goto, 1956). According to Iler the catalysts are required for formation of siloxane bridges between particles. Fluorine is important because it can substitute directly for oxygen. The catalytic effect of F^- and $(OH)^-$ ions is illustrated, as a function of pH, in Fig. 7. The maximum polymerization rate occurs between pH values of 5 to 8. In more basic solutions the increasing negative charge of colloidal particles overcomes the catalytic effect of increasing $(OH)^-$ concentration.

The rate scale in Fig. 7 is in arbitrary units. The following two

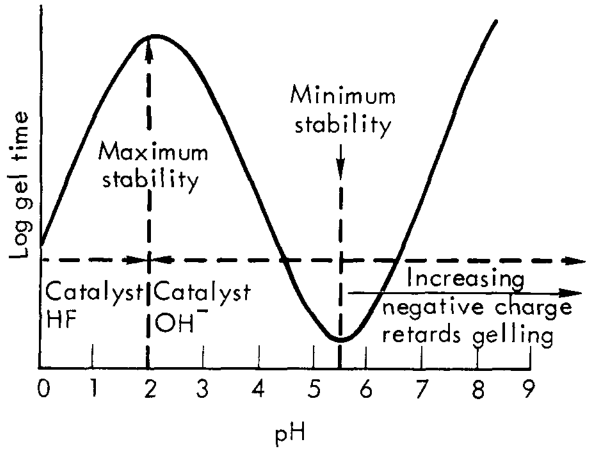


Fig. 7. Sol stability: relation between log (gel time) vs pH (reprinted from Iler (1955); copyright 1955 by Cornell University; used by permission of Cornell University Press).

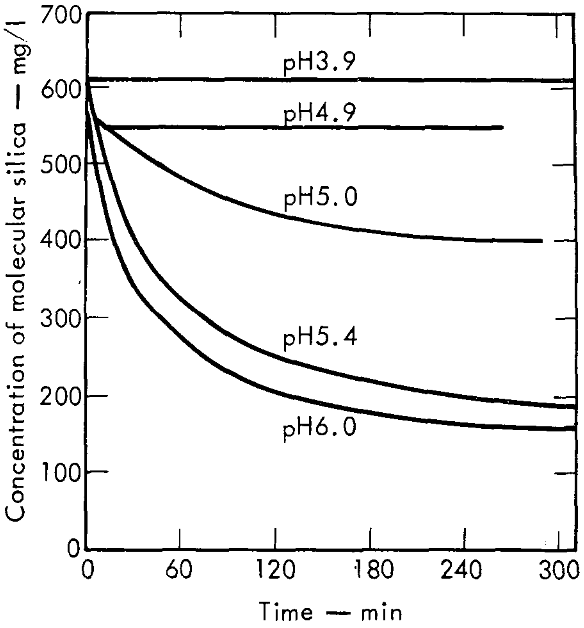


Fig. 8. Polymerization of silicic acid in acidic solutions (from Kitahara, 1960b).

examples illustrate the relationship between pH and rate of polymerization of supersaturated silica solutions.

Kitahara (1960b) produced saturated solutions of monomeric silica in a high-temperature pressure vessel and then quenched them to room temperature. He concluded that rates of polymerization were highest at pH 7.5. Above and below this pH value polymerization rates decreased (Figs. 8 and 9). At a pH of 4.9 or less, polymerization rates were negligible. With the exception of Goto (1956), previous work is in agreement with Kitahara (1960b). Goto (1956) concluded that both polymerization rates and particle size of colloidal silica increase with increasing pH. Kitahara (1960b) agreed that <u>initial</u> polymerization may occur more rapidly at high pH (7 to 9), but maximum rates are subsequently maintained at pH 7.5. As a second example, Treadwell (1935), reported that at a pH of 3.2, a 0.5 molar solution of disilicic acid

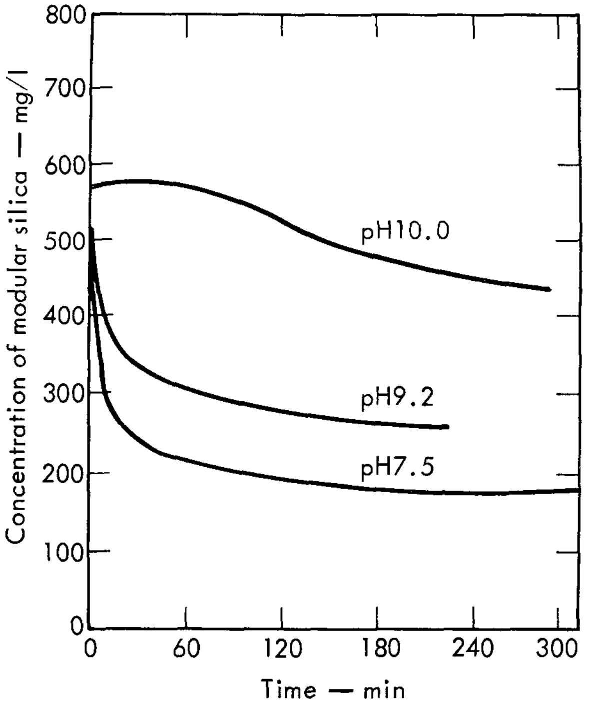


Fig. 9. Polymerization of silicic acid in basic solutions (from Kitahara, 1960b).

required 4 days to increase in molecular weight from 159 to 1500. Polymerization induced by increasing the pH of an acidic solution is not immediately reversible by reduction of pH. Alexander (1954) determined that a solution of monosilic acid will polymerize almost instantly at 0°C, when the pH of the solution is maintained between 5 and 6 for several seconds, and then lowered to pH 3.

In basic solutions, rates of silica polymerization increase with increasing salinity (Krauskopf, 1956). For example, at low temperatures (22 to 27°C), high concentrations of silica in alkaline solutions of sea water are rapidly (∿24 hr) reduced to the equilibrium value. As noted previously, above the isoelectric point (pH 1 to 3) the increasing concentration of hydroxyl ion promotes polymerization. Since cations can neutralize negatively charged colloidal particles, high salinities will accelerate their aggregation. At and below the isoelectric points, salts such as sodium chloride have little influence upon sol stability (Iler, 1955).

Polymerization rates of supersaturated solutions are inversely proportional to the second power of silica concentration at pH values in excess of approximately 3. In more acidic solutions, polymerization is a third-order reaction (Iler, 1955). Therefore, solutions with high initial degrees of supersaturation polymerize relatively rapidly to the equilibrium solubility. For example, White et al. (1956) reported that a hot-spring water sample with an initial supersaturation of 50% showed no significant polymerization in 4 months, while in another sample, with initial supersaturation of 200% (pH 7.3), 50% of the excess silica had polymerized within 24 hr. But even so, essentially no polymerization occurred during the first hour.

White et al. (1956) and Krauskopf (1956) also studied the effect of the presence of solid phases on silica solubility, Krauskopf reported the almost quantitative co-precipitation of colloidal silica by hydrous ferric oxide. White et al. noted that the presence of opaline sinter greatly increased the rate of polymerization of supersaturated solutions. However, neither ferric oxide nor opaline sinter affected monomeric silica in saturated solutions.

Fournier (1970), summarizing the work of Kato (1969), reported that dissolved silica will co-precipitate with hydroxides of iron and manganese. It has also been shown that even from undersaturated solutions (SiO_2 = 0.5 ppm) dissolved silica can be adsorbed by, and co-precipitate with, hydroxides of iron, aluminum, manganese, magnesium, and other elements (Harder and Flehmig, 1970; Schink, 1968; Iler, 1955). However, the reactions do not occur below the pH at which metal hydroxides would normally precipitate (Table 2). Adsorption may proceed by reaction of silanol groups with the metal hydroxides (Iler, 1955; Hazel, et al., 1949):

$$\mathrm{Si\ OH} + (\mathrm{Fe\ OH})^{+2} = (\mathrm{Si{-}O{-}Fe\ OH})^{+} + \mathrm{H}^{+}.$$

Iler (1955) notes that at pH values of 2 to 3 copper ion is not adsorbed by monomeric silica, suggesting that silanol groups cannot react with an ion such as $[Cu(H_2O)_4]^{+2}$ until a hydroxyl ion is incorporated into the coordination sphere of the metal.

Table 2. Precipitation of metal silicates.[a]

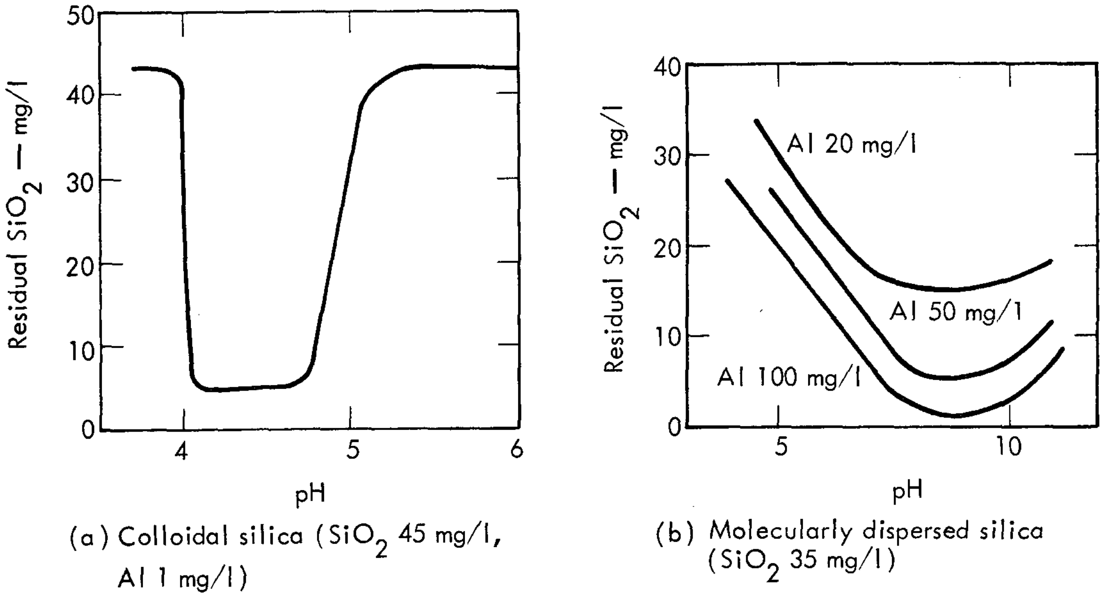
Solution titrated	Metal silicate precipitation began at pH	Metal silicate precipitation began at ml of sodium silicate	Hydroxide precipitation at pH
0.01 M. $ZrCl_4$	3.98	35.0	1.86
0.01 M. $ThCl_4$	3.50	30.0	3.50
0.001 M. $Al(SO_4)_3$	4.04	6.0	4.14
0.02 M. $BeSO_4$	5.31	20.0	5.69
0.02 M. $ZnSO_4$	5.25	1.0	5.20
0.02 M. $MnCl_2$	7.35	1.0	8.41
0.02 M. $MgSO_4$	9.50	1.0	10.49
0.02 M. $CaCl_2$	10.07	3.0	--

[a] The data were obtained by titration of 100 ml salt solutions with 0.1 N Na_2O 2.16SiO_2 solutions (Britton, 1927).

The work of Okamoto et al. (1957) serves as a good example of the influence of trace elements on both dissolved and colloidal silica. They determined that aluminum greatly decreased the rate of depolymerization of colloidal silica in an alkaline medium. Other experiments indicated the effect of pH and SiO_2-to-Al concentration ratios on the stability of colloidal silica, and solubility of monomeric silica. The optimum pH range for the essentially quantitative precipitation of colloidal silica from a solution with an SiO_2-to-Al ratio of 45:1 was 4.2 to 4.7 (Fig. 10). Neither colloidal silica nor aluminum precipitated at other than the optimum SiO_2-to-Al ratio of 45:1. The optimum pH and the SiO_2-to-Al ratio for precipitation of dissolved silica, however, were much different, about 9 and 1:3, respectively (Fig. 10). Unfortunately, the authors did not discuss the rates of precipitation or the nature of the silica-aluminum precipitate. However, they did refer to the work of Betz et al. (1940a) involving the removal of silica from boiler-feed water by co-precipitation with aluminum hydroxide.

Betz et al. (1940a) reported a reduction in dissolved silica from 18 to 4 ppm (78%) in 1 hr, by co-precipitation with aluminum hydroxide at 23°C and pH between 8.3 to 9.1. A similar reduction in dissolved silica (67%) was obtained at pH 7.6 to 8.0 with no residual Al remaining in solution. The authors indicated that co-precipitation of silica was less effective at higher temperatures. No precipitation of silica occurred at pH < 6.8. They concluded that precipitation of dissolved silica by aluminum hydroxide proceeds by adsorption.

Magnesium oxide was also found to be effective in the reduction of dissolved silica concentrations (Betz et al. 1940b). A 100% reduction in dissolved silica



(a) Colloidal silica (SiO_2 45 mg/l, Al 1 mg/l)

(b) Molecularly dispersed silica (SiO_2 35 mg/l)

Fig. 10. Co-precipitation of silica and aluminum (from Okamoto et al., 1957).

content (initial concentration 21.3 ppm) was achieved at 95°C and pH 10.1 in 15 min by co-precipitation with 300 mg magnesium oxide (added to a 3-liter solution as a slurry). The mechanism of silica removal from solution was thought to be by adsorption. Magnesium carbonate, in slurry form, was slightly less effective in the removal of dissolved silica from solution. An initial silica concentration of 21.0 ppm was reduced 86% in 15 min with 900 mg $MgCO_3$ added to 3 liters of solution (pH > 9). It has also been demonstrated that both anhydrous magnesium sulphate and ferric sulfate are capable of precipitating dissolved silica (Behrman and Gustafson, 1940).

Rates of polymerization (and dissolution) increase with increasing temperature (Krauskopf, 1956; Kitahara, 1960b; Fournier, 1970). While several months might be required to reach equilibrium solubilities at low temperatures, with respect to either quartz or amorphous silica (see Fig. 5), at elevated temperatures saturated solutions can be obtained in 4 hr to 4 days (Hitchen, 1935; Kennedy, 1950; Morey et al. 1962; Fournier and Rowe, 1962).

Goto (1956) gives the following equation for the rate of polymerization of dissolved silica:

$$-\frac{dc}{dt} = k\ (C - C_e)^n ,$$

where:

C = concentration of monomeric silica,

C_e = equilibrium concentration of monomeric silica at a particular temperature,

k = rate constant,

n = order of reaction.

Kitahara (1960b) reported that n=2 in acidic solutions and n=3 in alkaline solutions. His plots of monomeric silica concentration and -log k as functions of time and 1/temperature, respectively, indicated that polymerization rates increase with increasing temperatures (Figs. 11 and 12).

Summary

The important conclusions to be drawn from this review of the aqueous chemistry of silica are:

1. The primary aqueous silica species in saturated solutions of pH less than 8.5 to 9 is the monomer, H_4SiO_4.
2. Amorphous silica controls the solubility of orthosilicic acid (H_4SiO_4).
3. The rate of polymerization of silica is pH-dependent. Polymerization rates are highest at pH 7.5, but are lower in acidic or more alkaline solutions. Minimum rates of polymerization occur at pH values of 1 to 3. For example, amorphous silica does not precipitate from solutions of sea water (temperature = 22 to 27°C; pH = 4.9) with initial degree of supersaturation, with respect to amorphous silica, of about 150%. Below 100°C, the polymerization rate has been shown to be accelerated by NaCl for solutions with pH > 7. In acid solutions, electrolytes do not influence polymerization rates.
4. The polymerization rate of a supersaturated silica solution increases with increasing temperature.
5. Dissolved silica can be effectively removed from solution by coprecipitation with MgO_2, $MgCO_3$, Fe-, Al-, Mg-, and Mn-hydroxides, and by magnesium and ferric sulphates. Colloidal silica can be coagulated by electrolytes of sea water, and essentially quantitatively precipitated by aluminum and hydrous ferric oxide. The rate of polymerization of supersaturated solutions and precipitation of colloidal silica is accelerated by the presence of solids.
6. Supersaturated solutions (pH $\leq$ 7), when cooled by passage through a steel condenser tube, show no tendency to precipitate amorphous silica.

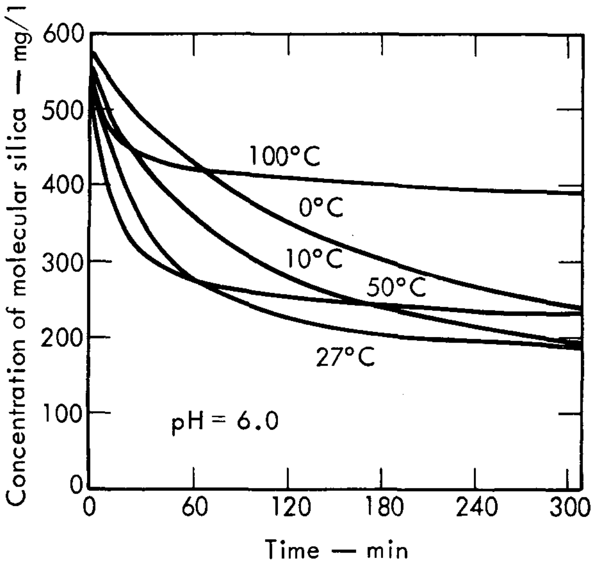


Fig. 11. Temperature dependence of rate of polymerization of silicic acid (from Kitahara, 1960b).

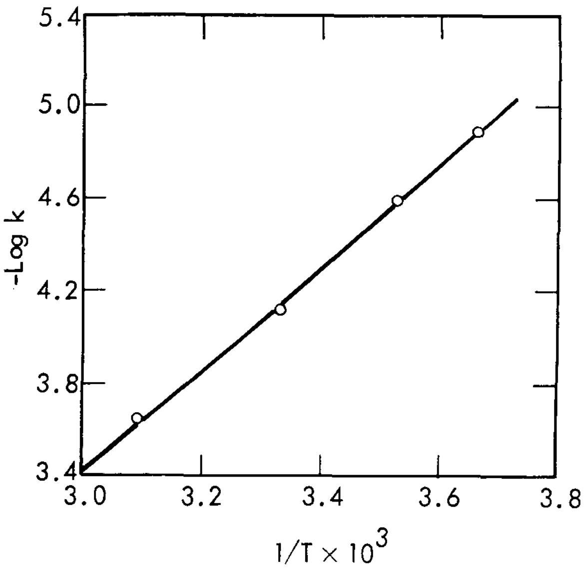


Fig. 12. Variation of polymerization rate constant k with temperature (from Kitahara, 1960b).

Mechanisms Controlling Precipitation of Amorphous Silica From Salton Sea Geothermal Field Brines

Source of Silica in SSGF Brines

The sediment fill of the Salton Trough consists primarily of silts, fine-grained sands, and muds deposited as part of the Colorado River delta (Muffler and White, 1969). Quartz is undoubtedly a major constituent of these sediments. Helgeson (1968) indicated that the highest temperatures in the SSGF were measured in the Elmore No. 1 well (∿ 360°C). If it is assumed that the brines are in equilibrium with quartz, Fig. 1 indicates that the dissolved silica content of the brine should be about 500 ppm. White (1968) reported 400 ppm silica for Imperial Irrigation District (IID) No. 1 and No. 2 wells (corrected for steam loss). The agreement between empirical and observed silica concentrations is reasonably good, and suggests, therefore, that dissolution of quartz is the primary control on the silica content of the brines.

Precipitation of Amorphous Silica From SSGF Brines

With the review of the aqueous chemistry of silica completed, it will now be of interest to analyze the effects, relative to the precipitation of amorphous silica, of expanding the brine from 300°C (assumed reservoir temperature) to 50°C (total flow turbine exhaust temperature). For the purposes of this discussion, it will be assumed that the "brine" is water (pH 4.5 or less) saturated with respect to quartz at 300°C (∿ 630 ppm H_4SiO_4). According to Austin *et al*. (1973), the steam quality of a typical total flow system operating on brine from a 300°C reservoir is about 37% at the exhaust. This quality corresponds to an effective silica concentration of 1000 ppm in the brine at 300°C. Since the primary aqueous silica species in acidic waters is the monomer, H_4SiO_4, and since amorphous silica controls the solubility of dissolved silica, no precipitation should occur until the brine temperature falls to about 230°C (see Fig. 1). At 50°C, the degree of supersaturation of the brine, with respect to amorphous silica is about 400%. However, so long as the pH does not rise above 4.5 the rate of polymerization of monomeric silica will be low, and immediate precipitation of silica should not occur.

It is concluded, therefore, that simple silica solubility equilibrium relationships cannot account for the precipitation of amorphous silica from SSGF brines.

Scale Formation

No studies are available in the literature that describe the formation of SSGF opaline-sulfide scale as a function of decreasing temperature and pressure. However, it has been established, from observation of scale morphology and composition, that sulfides precipitate before amorphous silica (Skinner *et al*. 1967; Austin, 1975). Arborescent growths of sulfides, curved inward in the direction from which the fluid flowed, have been described by both Skinner et al. (1967) and Austin (1975). The unaltered condition of dispersed sulfide phases is evidence for the subsequent growth of protective layers of silica in intersticial spaces. The amorphous silica has also been shown, on the basis of its high index of refraction, to contain up to 5.4 wt% iron, and 6.0 wt% sulfur (Skinner et al. 1967). Authigenic crystalline silicate phases have not been reported in SSGF scale.

It is important to identify those elements that are selectively fractionated into precipitated phases. Partition coefficients can be defined for this purpose as the ratio of the concentration of an element in the brine to its concentration in precipitates formed from the brine. Computed partition coefficients for precipitates formed from Sinclair No. 4, and a Magma Power well brine are given in Table 3. Chemical analyses for brine from IID No. 1 and IID No. 2 wells were used to compute an average brine composition.

Although the absolute values of these partition coefficients are meaningless, their relative magnitudes clearly indicate whether an element fractionates into the solid phase. For example, scale has been reported with aluminum and magnesium concentrations up to 30,000 and 5000 ppm, respectively, although their average concentrations in brine are low (Skinner et al. 1967; Lim and Peck, 1974; Lim et al. 1974). As a consequence, their partition coefficients are less than 1.0.

Table 3. Partition coefficients for elements in SSGF brine.

Element	Average brine[a]	Brine Precipitate[b]	Brine Precipitate[c]
Na	51,700	5.17	10.34
K	17,000	3.40	---
Ca	28,400	2.84	5.68
Ba	242.5	1.21	1.21
Mg	32	0.11	0.06
Mn	1385	0.35	0.69
Al	4.2	0.00014	0.0021
Fe	2145	0.022	0.054
Cu	5.5	0.00011	0.014
Zn	520	1.73	0.17
Pb	91	0.018	0.0005
Ag	1.4	0.00007	0.00004

[a] Average computed from brine analyses for IID No. 1 and IID No. 2 wells (White, 1968).

[b] Chemical analyses for precipitates are from Lim et al. (1974).

[c] Magma power well precipitate.

Silica Precipitation Mechanisms

A simple model is proposed to account for the precipitation of amorphous silica from SSGF brines. Because of the lack of information bearing on the kinetics of scale formation, the model should be viewed as a working hypothesis. As more data become available necessary refinements can be made. The ultimate goal will be to achieve a basic understanding of precipitation mechanisms, at which time it may be possible to devise methods for minimizing or preventing the problem.

As brine is expanded to the surface from a geothermal reservoir, it cools adiabatically. As pressure declines, dissolved gases and steam are evolved, and the residual brine salinity increases. The principal result of the evolution of CO_2, the most abundant noncondensible gas in SSGF brine, and H_2S is an increase in brine pH. As a consequence, sulfides (and probably hydroxides of multivalent elements, such as iron, aluminum, zinc, lead, possibly rare earths, etc.) begin precipitating. A suite of dispersed fine-grained sulfides (and hydroxides) induces the precipitation of dissolved silica either by serving as nucleation centers or by adsorption mechanisms.

The presence of NaCl promotes the polymerization of monomeric silica in basic solutions. Simultaneous increase in pH and decrease in temperature, coupled with high concentrations of NaCl, KCl, and $CaCl_2$, probably induce polymerization of silica in SSGF brines when brine pH values exceed 4.5.

Lim (1974) obtained experimental evidence that supports the hypothesis that sulfides and hydroxides co-precipitate dissolved silica from SSGF brines. A mixture of black and clear gelatinous precipitates formed within 15 min after a quenched Sinclair No. 4 brine sample (temperature 24°C) was opened and placed under a nitrogen overpressure to avoid atmospheric contamination. The pH of the brine solution increased from 4.5 to 6.7 over a period of several hours.

The precipitated phases were not identified, but on the basis of his chemical analyses it is probable that the black phase was a sulfide, and the clear gelatinous material was amorphous silica. The slow rise in pH of the solution can be attributed to the evolution of CO_2 and H_2S after the sample bottle was opened. The critical observation is that silica did not precipitate from the brine, which was supersaturated with respect to amorphous silica, until formation of the black precipitate and pH increase.

Subsequently, Lim exposed the filtered residual brine to the atmosphere. $Fe(OH)_3$ co-precipitated additional silica. The final silica content of the remaining brine was only 34 ppm, a concentration well below the solubility of amorphous silica at room temperature ($\sim$ 100 ppm).

Summary and Conclusions

The precipitation of amorphous silica from SSGF brines cannot be explained in terms of simple solubility equilibrium relationships. Silica precipitation is promoted by several independent mechanisms. Release of pressure and evolution of CO_2 and H_2S result in an increase in residual brine pH from a nominal value of between 4 and 4.5 to 5 or higher. As a consequence, dissolved silica polymerizes more rapidly and is co-precipitated by sulfides and hydroxides. At higher pH values ($\geq$ 5) sodium-, calcium-, and potassium chlorides promote the polymerization of monomeric silica. Any colloidal silica that appears in solution is either coagulated by electrolytes or precipitated by solid phases including particulates derived from the pro-producing formation.

The utilization of SSGF brines by a total flow or other energy-conversion system will necessitate minimizing or preventing precipitation of solid phases and subsequent scale formation. Since supersaturated silica solutions polymerize more rapidly at higher temperatures and pH ($\geq$ 5), it is concluded that it may be possible to retard, if not prevent, precipitation by controlling brine pH and expediting its flow from the wellhead through the power plant equipment. Acidification may also prevent initial sulfide and hydroxide precipitation.

The effectiveness of acidification, as a means of stabilizing supersaturated silica solutions, has been demonstrated for Cerro Prieto geothermal brines. After steam separation, residual brine contains over 1000 ppm silica, which can be kept in solution for up to one month by maintaining the pH between 0 and 1 with nitric acid (Reed, pg. 35, 1974)! The viability of any proposed additive for brine modification is ultimately dependent upon its cost. If an average flow rate of 500 lb brine/sec is assumed (the flow from four wells required to produce 44 MW of electricity — Austin *et al*. 1973), 2.1 tons per day of concentrated hydrochloric acid will be required to maintain the pH of SSGF brine at a value of 3. Assuming the availability of commercial grade hydrochloric acid (31% by weight) at \$50 to \$60 per ton, the maximum cost per day is \$126 or 0.12 mills/kW hr. The cost of an hydrochloric acid additive is, therefore, acceptable.

Direct reinjection of spent brine is not advisable if precipitation cannot be prevented. Even if the brine were reheated to ambient reservoir temperatures instantaneously, the time required for dissolution of precipitates may be relatively long. For example, several hours are required to produce saturated silica solutions by dissolution of amorphous silica in high-temperature bombs. If the average radii of precipitates exceeds pore space radii, formation sealing will be inevitable. A practical reinjection system might involve the use of temporary holding ponds. Exposure of brine to atmospheric oxygen will result in precipitation of hydroxides, oxides, and silica. Since these precipitates may also be enriched in iron, copper, silver, etc., this type of system has the potential for integration into a mineral recovery operation. On the other hand, if acidification completely prevents precipitation, direct reinjection of residual brine may be feasible.

Acknowledgments

The author wishes to thank J. H. Howard, D. D. Jackson, P. W. Kasameyer, A. W. Lundberg, and R. N. Schock for their assistance.

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