KINETICS OF SILICA DEPOSITION

FROM SIMULATED GEOTHERMAL BRINES

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Summary

In our experiments supersaturated brines were passed through columns packed with several forms of silica (crystalline α quartz, polycrystalline α quartz, and porous Vycor). Also, silica deposition on ThO_2 microspheres and titanium powder was studied under controlled conditions of supersaturation, pH, temperature and salinity. The residence time was varied by adjustments of flow rate and column length. The silica contents of the input and effluent solutions were determined colorimetrically by a molybdate method.

The following observations have been made:

1) Essentially identical deposition behavior was observed once the substrate was thoroughly coated with amorphous silica and the BET surface area of the coated particles was taken into account.

2) The reaction rate is not diffusion limited in the columns.

3) The silica deposits from a solution containing only monomeric $Si(OH)_4$.

4) The deposition on all surfaces examined was spontaneously nucleated.

5) The dependence on the supersaturation concentration, hydroxide ion concentration and temperature were determined.

The empirical rate law which describes our data in 1 m NaCl in the pH range 5-7 and temperatures from 60-100°C is:

$$-\frac{d[Si(OH)_4]}{dt} = 0.12 \ A \ ([Si(OH)_4] - [Si((OH)_4]_{eq})^2 \ [OH^-]^{0.7} \qquad (1)$$

where A is the surface area in cm^2 SiO_2 per kg of water in column voids, t is in minutes, and the concentrations are in molal units. Hydroxide concentration was derived from the measured pH and the ionization quotient for water. In the expression given above the rate constant is essentially independent of temperature over the range 60-100°C. Alternatively the rate of linear growth

of an amorphous silica surface in cm/min is given by

$$\frac{dh}{dt} = 3.1 \; ([Si(OH)_4] - [Si(OH)_4]_{eq})^2 \; [OH^-]^{0.7} \tag{2}$$

These results allow one to make estimates of deposition rates when information about the available area of amorphous SiO_2, the supersaturation, the pH and temperature are known. These studies will be extended and applied in interpreting silica scaling results in a dynamic system at ORNL.

1. Introduction

1.1 General (Behavior of Silica)

The mode of occurrence of silica in dilute aqueous solutions is generally accepted to be as the species $Si(OH)_4$ in the acidic-to-neutral pH range. In basic solutions the anionic species $SiO(OH)_3^-$, $SiO_2(OH)_2^{2-}$, and $Si_4(OH)_{18}^{2-}$ have been observed[1,2] in potentiometric studies. The equilibrium reactions amongst these anions and the neutral silicic acid have been studied in detail in sodium chloride solutions to 300°C. Also, the fluoride ion interacts with silicic acid in relatively acidic solutions, producing principally the SiF_6^{2-} complex.[3] The stability of the complex decreases as the temperature increases.

The solubility in water of the most rapidly precipitating solid form, amorphous silica, has been investigated by Fournier to 350°C.[4] The solubility to 250°C at the saturation vapor pressure is represented in molal units by the expression

$$\log[Si(OH)_4] = -0.26 - 731/T \tag{1}$$

It is generally accepted that in equilibrium with amorphous silica (and also for the more insoluble crystalline phases of silica--quartz, crystobalite, etc.) the principal silica present in acidic solutions is monomeric silicic

acid (possibly with some dimeric). This is based on the rapid color development in the molybdate method of analysis and also on analysis of potentiometric data in nearly saturated solutions.[1,2] However, when the solution phase is supersaturated with respect to amorphous silica, polymerization proceeds with formation of colloidal particles and ultimately amorphous silica precipitates. The most regularly formed amorphous silica is natural opal consisting of a lattice-like structure of primary and secondary spheres.[5]

The polymerization process has been studied extensively, and most recently by Makrides et al.[6,11] who have also reviewed the previous work. The results of their work will be summarized briefly in a later section. There is now considerable information on the nucleation process and initial stages of growth, but insufficient information exists to permit an analytical description of the growth process either from homogeneous solution or onto preformed and well characterized surfaces. It was the objective of this present work to conduct laboratory studies which would provide this kinetic information. The work is part of a program at Oak Ridge National Laboratory to examine silica deposition behavior in dynamic geothermal systems from hydrothermal brines which are found in the western United States.

1.2 Geothermal Scaling

The principal materials[7,8] deposited from geothermal brine as the heat is extracted are $CaCO_3$, metal sulfides, and amorphous silica or mixed phases in an amorphous matrix. The deposition of calcium carbonate is rapid when supersaturation conditions exist as a result of the removal of CO_2. The kinetic behavior of silica is much less predictable because of slow nucleation behavior. When the brines are extracted from deep hot reservoirs, the silica content corresponds to the solubility of α-quartz in the brine at the

reservoir temperature.[9] Because of the very slow kinetics of crystalliza-
tion of quartz below 300°C, silica is deposited during the heat extraction
process as the more soluble amorphous form. Considerable supersaturation
(often several times the equilibrium solubility) occurs and the factors
which affect the kinetics of deposition are the subject of this paper.

In our view, controlling conditions to prevent nucleation is generally
impractical in the complex natural brines with their variable composition and
suspended solids and high supersaturation values. For this reason we have
chosen to define the kinetics of the deposition of silica onto amorphous silica
surfaces whose areas are known. In other words, we are examining the growth
process rather than the nucleation process. With sufficient kinetic informa-
tion, the design of the extraction process can be chosen to minimize the impact
of deposition of such scales.

1.3 Polymerization of Silica

The disappearance of monomeric silica from solution as evidenced by
analyses by the molybdate method has been the principal method of study of the
polymerization process. The most carefully conducted and authoritative work
on silica polymerization is that of Makrides et al.[6,11] Their results have
shown that the polymerization proceeds through nucleation and growth stages
which are influenced principally by the supersaturation, the pH and the salt
concentration. Qualitatively, the disappearance of monomeric silica with
time exhibits a plateau or induction time during which nuclei are formed;
this is followed by a period of rapid reaction and subsequent gradual
approach to the silica concentration corresponding to the equilibrium
solubility of amorphous silica at the conditions of the experiment.

Quantitatively the induction or nucleation time τ (min) is expressed as[*]

$$\ln\tau \simeq \ln\left[\frac{1}{\ln(\underline{m}/\underline{m}_e)}\right]^8 + 4.8 - 2.3 \ (pH - 4.5) \tag{2}$$

independent of temperature (75-105°C) within the experimental error. The

effect of salinity of the solution on the nucleation rate was viewed by the

authors as originating principally through the salt effect on m_e, the equi-

librium solubility of the silica. Other effects can also be anticipated such

as the salt effect on the activity coefficients of $Si(OH)_4$ and the hydroxide

ion. Obviously, the nucleation rate or induction time is a very strong function of

the supersaturation ratio and at high pH values the rate is fast enough to

occur during the hold-up in process equipment. The kinetics of nucleation

and initial growth have been discussed[11] in terms of a model which we feel

is oversimplified. Although the growth is considered to be interface-

controlled, the assumed first order reaction is not consistent with our

observations to be reported here.

1.4 Kinetics of Crystal Growth

The theory on crystal growth is not yet at a stage where the mechanism of

growth or the form of kinetic rate law are predictable[12,13,14] unless the

process is under diffusion control. The growth rate for some substances is

indeed limited by diffusion in solution, but for others it is limited by inter-

face reactions. Since in the case of silica deposition the process is accom-

panied by dehydration, one might expect interface reaction limitation.

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[*]This expression was derived from the data given by Makrides et al. in Fig. 17.

Fick's first law of diffusion describes the heterogeneous processes which are diffusion limited, i.e.,

$$J = -D\frac{\Delta m}{\Delta X}A \tag{3}$$

where J is the flux of deposition (moles kg^{-1} sec^{-1} cm^{-2}), Δm is the concentration gradient across the film of thickness ΔX and A is the surface area per kilogram of water.

Where interface reactions are limiting the form commonly observed is

$$-\frac{dm}{dt} = kA \ (m - m_e)^n \tag{4}$$

where k is a specific rate constant, A is the area of the solid per kg of solution and m_e represents the molal solubility of the substance. The order of the reaction depends on the number of ions involved in the formula of the salt. There is not yet a very satisfactory explanation for this mathematical form with respect to the concentrations, but the most often quoted one was put forth by Doremus.[15] In his work on ionic salts, n took values of 3 and 4 depending on the number of ions in the crystal. The essential part of his detailed interpretation is that the rate limiting step involves adsorption of the reacting species on the surface and that this adsorption is proportional to the difference $m - m_e$.

1.5 The Packed Column Approach

In this program we have packed small columns with various substrates of known BET surface areas and then passed solutions supersaturated with silica to coat the substrates with amorphous silica. Then we examined the kinetics of deposition on the coated surfaces and measured the BET surface areas when the experiment was completed.

The use of a packed column has several advantages in studies of this type. The principal advantages are:

1) The high surface area-to-volume ratio which allows the deposition on the bed to occur to the exclusion of homogeneous nucleation and polymerization in solution;

2) The ease of sampling and quenching which are essential when the residence times are short (minutes);

3) The elimination of agitation and possible attrition caused by stirring as in a batch equilibration.

2.   Experimental

2.1 Apparatus

The brine preparation and packed column setup are shown in Fig. 1. Brine of appropriate composition was pumped through a preheater and saturator column with the saturator column held at the temperature required to give the desired silica concentration. The silica saturated brine thus prepared then passed through a manifold held at the same or a slightly higher temperature to prevent premature polymerization; a sampling station provided for monitoring the silica concentration in the brine. Connections from the manifold to the packed columns and their individual effluent samplers were made with titanium capillary tubing and minimum holdup valves to minimize extraneous volumes. The columns and a temperature adjustment coil were immersed in thermostatted baths as shown. Initially the columns were 9.5 mm ID Pyrex pipe, but later 8.4 mm ID titanium pipe was used. The effluent was initially quenched in a capillary coil in an ice bath; our experience has shown this to be an effective way to prevent capillary and valve plugging. The samples were taken in volumetric flasks containing an aliquot of hydrochloric acid solution such that the pH of the mixture was between 2 and 3; supersaturated silica brines such as we have dealt with are stable for hours in this pH range.

2.2 Substrates

Several substrates have been used in these studies, including:

Polycrystalline α quartz - aggregates of small angular grains individually less than 9 μm in diameter; aggregates average 70 μm and range to 350 μm. Fines were separated from the material used in the columns by Stokes column flotation with flow rates designed to remove particles smaller than 25-50 μm. Several percent of single crystal particles in the same size range (50-350 μm) were also present, as were some magnetic iron oxide particles.

A semiquantitative analysis of this material showed the following in addition to Si (in ppm): Al-400, Ca-20, Cr-5, Cu-10, Fe-1000, K-50, Mg-10, Mn-100, Na-30, P-25, U-5, Zn-5. The material was obtained from a mine in southern Illinois and was reported to be amorphous, but X-ray diffraction showed it was α quartz, as was also indicated by solubilities encountered in attempting to use it as a charge for our saturator column. Some other characteristics for this, and the other substrates used in the kinetic studies, are given in Table 1.

Monocrystalline α quartz - single crystal material consisting of rounded grains ranging from 120 to 800 μm across. Under the microscope the material appeared appreciably cleaner and purer than the polycrystalline α quartz.

Porous Vycor - this is the same material as used in our saturator column. It was ground and sieved (-140, +200 mesh) and is amorphous silica containing about 3% B_2O_3 after leaching to give high porosity.

Powdered titanium metal powder - (-50, +100 mesh) and reported to be 99.7% Ti by the supplier.

Thoria microspheres - 210 to 240 μm spheres of very pure polycrystalline thorium oxide prepared by the sol-gel process.

2.3 Column Preparation

Initial silica deposition on the columns is very much a function of the characteristics of the substrate, particularly the original surface area. Thus, the porous Vycor with very high (164 m^2/g) surface area quickly reduced the silica concentration in the column effluent to the equilibrium solubility at the temperature of operation; the materials with low area (0.03 m^2/g) monocrystalline α quartz and the thoria microspheres, on the other hand, removed very little silica during early column operation. The substrates with intermediate areas, polycrystalline α quartz and titanium powder, showed intermediate removal. Homogeneous polymerization during overnight shutdowns, when these occurred, may have played a part.

During the first few tens of hours of column operation, the removal of silica by a column was quite erratic. After a time, however, depending on conditions, all substrates were "coated" with amorphous silica and gave quite reproducible results. The effluent SiO_2 concentration during "coating" of a polycrystalline α quartz column is shown in Fig. 2. During the first three days of operation the results were erratic. However, after the substrate was fully coated with amorphous silica, reproducible results were obtained as a function of residence time. At that stage, as shown in Fig. 3, the relation between the silica removed by the column and residence time became quite reproducible. The data at each of the three pH's are quite reproducible even though duplicate runs were carried out on different days and with different length columns.

2.4 Measurements and Calculations

The pH (minus the logarithm of the hydrogen ion molality) measurements were based on a standard containing 0.01 m HCl in 1.0 m NaCl and the hydroxide concentration was calculated using the known ion product of water in 1 m NaCl.[16] Individual measurements are accurate to about 0.05 log units.

Silica was determined by a procedure developed from that described by Grasshoff.[17] Three stock solutions are used:

a) 2 M $(NH_4)_2 SO_4$, pH 3.0

b) 35.6 g $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$ per liter

c) 1.5 M Cl CH_3 COOH, pH 3 with NH_4OH

These solutions are mixed in the volume proportions 5:2:2 for a, b, and c and filtered. The mixture is added to 1 cm^3 of the unknown in a 50 cm^3 plastic volumetric flask and the color development measured at 390 nm after 10 minutes. The silica concentration was calculated from standards with 250 and 500 mg/kg H_2O which were checked daily. The mixture can be used during an eight hour day but may get hazy standing overnight. The pH of the final mixture should be between 3.0 and 3.2. In those samples where some polymerization had taken place, total silica was determined by digesting the 1 cm^3 sample aliquot with an equal volume of 30% NaOH for several hours or overnight, and neutralizing the NaOH with 1 cm^3 of concentrated HCl (with the volumetric flask in an ice bath) just before adding the molybdate mixture. We estimate an overall analytical error of ± 10 mg/kg H_2O.

The residence time in columns was established by dividing the column void volume by the measured flow rate in cm^3/min.

The weighting factors used in least squares analyses were obtained by assigning errors of (±10 mg/kg H_2O) to each silica determination in the term $(\underline{m} - \underline{m}_e)^{-1}$.

Surface areas were determined with a Digisorb 2500 Multigas Surface Area Analyzer by the Micromeritics Laboratory of the Y-12 Plant.

3. Results

3.1 Silica Concentration

Earlier studies of silica polymerization, wherein the molybdate reactive silica was followed and where the number of reactive sites of the polymerized silica was unknown, have found widely varying dependence on the silica concentration. The most often cited reaction order has been third with respect to the supersaturation concentration, i.e., the concentration of monomeric silicic acid in the solution of interest minus the equilibrium solubility of amorphous silica in that solution; however, orders ranging from 0 to 3 have been reported by various investigators.[18] Thus, the determination of the reaction order for the deposition of silica from supersaturated brines was the first subject investigated.

First order behavior in supersaturation, $(m - m_e)$, is not indicated by the semi-log plots shown in Fig. 4. The values for m_e were taken from solubility measurements by Marshall[19] for amorphous silica in salt solutions at these temperatures. Higher orders (2 and 3) were examined using the general equation described below. Data were fit with the integrated form of the following general rate expression (at constant pH)

$$\frac{-dm}{dt} = k' \, (m - m_e)^n \tag{5}$$

which gives

$$\frac{1}{(m - m_e)^{n-1}} = \left[\frac{1}{(m_o - m_e)^{(n-1)}} \, k' \, t \right] \tag{6}$$

where n is the order with respect to the supersaturation for n > 1, m is the

molal concentration of dissolved silica ($Si(OH)_4$) in the column effluent, $\underline{m}_e$ is the equilibrium solubility of amorphous silica in the salt medium solution at temperature, and t is the residence time in the column. Second-order plots for three different pH values at 60°C are shown in Fig. 5. The agreement factors for a number of column runs are tabulated in Table 2. While not uniquely so, the second order reaction is strongly favored by these data. Data for column studies carried out are summarized in Table 3. The rate constants were calculated using the second order rate law in terms of silica concentration. Dependence on the other parameters investigated is discussed below.

Hydroxide Concentration. The rapid acceleration of silica polymerization with increasing pH has been reported by a number of investigators.[20,21,22] Silica deposition has also shown similar behavior. From the data of Table 3 for polycrystalline quartz and several pH values the specific rate constant was evaluated from the relationship

$$k' = kA[OH^-]^P \tag{7}$$

where A is the BET surface area of the coated material in cm^2 per kg of water in the voids of the column bed. The variation approaches an order of magnitude per pH unit and is consistent with the polymerization data of Makrides et al.[6,11] The hydroxide ion concentration used in the calculation of the specific rate constant in the last column of Table 3 was derived from the measured pH and the ion product of water in the brine at the temperature of the experiment. The exponent or order of the $[OH^-]$ term in the rate expression was obtained from a least squares fit of data obtained with columns at pH values of 5.25, 6.00 and 6.76. Both the rate constant and the order for the hydroxide were allowed to vary in obtaining the value of 0.70 ± 0.16 for p.

Surface Area. The surface area of the substrate is, of course, a signi-
ficant factor in the reaction rate. The area to be considered, however, is
that which was present after the original substrate was coated as described
previously. We have used the BET surface areas determined by nitrogen or
krypton adsorption after drying the column material at 125°C. The results
for polycrystalline quartz, titanium powder and thoria microspheres are re-
markably consistent when the surface area is taken into account. The rate
constants computed for porous Vycor are much too low compared to these
materials and suggest that large amounts of the internal area is unavailable
for silica deposition. We have no ready explanation for the somewhat higher
rate constants shown in Table 3 for the monocrystalline quartz.

Temperature. The data in Table 3 show no effect of temperature
(60 to 100°C) when resultant changes in hydroxide ion concentration are
taken into account.

4. Discussion

Many investigators have found that the polymerization of silica from
supersaturated brines is substantially enhanced as the supersaturation, pH,
and salinity are increased. The same parameters are generally regarded as
having similar significance in the deposition of amorphous silica scales from

supersaturated brines. Additional constituents which have been discussed are fluoride[12], sulfides[23], and other mineral species found in silica scales[24]. Our studies, consistent with other observations, have shown that hydrodynamics also plays a significant role, e.g., valves are more prone to scale than pipe runs[20].

Early concerns of these column studies addressed the questions:

Which species are involved in the deposition reaction?

Is the process under diffusion or interface reaction control?

4.1 Identity of the Depositing Species

The first of these questions was addressed by conducting experiments in which only monomeric silicic acid (rapid molybdate reaction species) was present in the input solution under conditions where no significant poly-merization occurred during the residence time on the column. We found that under various conditions more than half of the silica was deposited directly from the monomer solution. In other experiments we examined the relative deposition of monomeric silica and polymerized silica from the same solution. Again, the monomeric species was shown to be depositing while there was little or no tendency for deposition of the previously polymerized silica. Interestingly, the deposited material often occurs as interlaced spheroids which are well cemented by a fine matrix.

4.2 Deposition Rate Control

There are three kinds of evidence that the deposition process is not diffusion (in the liquid phase) controlled: 1) the slow equilibration rate in a packed bed, 2) the independence of silica deposition on flow rate in a packed bed, and 3) the dependence of the rate on hydroxide concentration.

In applying the first of these criteria the equilibration time expected in a stationary liquid phase in a packed column was estimated using the method of Kraus et al.[25]
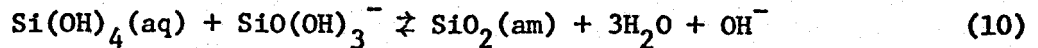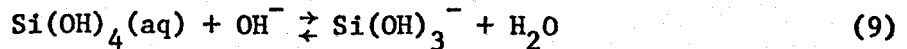
$$\tau < (R^2/D) \ [-0.05 - 0.233 \ \log \Delta] \qquad (8)$$

Assuming $R \sim 0.005$ cm, $D \sim 10^{-5}$ cm^2/sec and Δ (the complement of the fractional attainment of equilibrium, e.g., 0.01 for 99% of equilibria), the value of τ is less than 1 sec for Δ of 0.01 or 0.05 sec for Δ of 0.5. Of course, in a flowing system one would expect lower equilibration times because of the thinner diffusion layer. In all our experiments equilibration times were much greater ($>10^4$ times) than the values estimated above.

In a flowing system the diffusion film thickness is related to the flow rate, yet we observed no dependence of the equilibration time or silica removal on flow rate when the residence time was kept constant by changing the column length.

The dependence of the kinetics on hydroxide concentration, to be discussed later, also shows that the process is reaction limited.

4.3 Mechanism of Deposition

Although it has been demonstrated by this work that monomeric silica will deposit directly without necessarily previous polymerization, little else can be deduced from the observed kinetics. There has been no satisfactory explanation for the commonly observed crystallization kinetics showing greater than first-order dependence on the supersaturation concentration. Since the data were best fit with an order of 0.7 ± 0.16 for the hydroxide concentration, the predominant process can reasonably be thought of as hydroxide catalyzed. In the case where $\underline{m}$ approaches $\underline{m}_e$, the observed kinetics is consistent with the following simple processes:

$$Si(OH)_4(aq) + OH^- \rightleftharpoons Si(OH)_3^- + H_2O \qquad (9)$$

$$Si(OH)_4(aq) + SiO(OH)_3^- \rightleftharpoons SiO_2(am) + 3H_2O + OH^- \qquad (10)$$

where the first is the simple ionization equilibrium and the second is a bi-molecular step in which the catalyst, hydroxide ion, is regenerated. This process leads to a rate law of the form

$$\frac{-dm}{dt} = k(\underline{m}^2 - \underline{m}_e^2)[OH] \qquad (11)$$

which approaches the observed dependence on supersaturation as $\underline{m}$ approaches $\underline{m}_e$.

The pH or hydroxide dependence suggests the participation of the silicate species as was also suggested by Makrides et al. for the polymerization studies.

4.4 Applications

With Eq. (5-7) one can estimate silica deposition rates on previously coated surfaces. Fig. 6 illustrates that a maximum rate is observed at constant pH as the temperature increases; this results from the opposing effects of rapid increase in hydroxide concentration (from the changing ion product for water) and the decreasing supersaturation. The position of the maximum also increases sharply and shifts toward higher temperatures as the silica concentration increases. The model represents the condition where short residence times are considered and homogeneous nucleation is not a competing process. By incorporation of the model for homogeneous nucleation and kinetic behavior at the early stages of polymerization presented by Makrides et al., one could model more complex real systems. However, many details such as heterogeneous nucleation behavior and the specific effects of partially covered substrates on growth rates are not known. The rate of change of specific area of the coated deposit with deposition and the relationship between the surface area of the deposit and the surface area of the substrate are also unknown at this time.

With the possibility of prolonged contact with natural silicates and silica, one would predict rapid plugging of underground formations; this is a principal concern regarding the reinjection of waste geothermal brines. From the kinetics reported here we calculate that the linear growth rate of a surface at pH of 7 at 100°C and supersaturation of 0.006 m (360 ppm) is 0.6 μm per day. Such rates will reduce porosity in the vicinity of the reinjection and likely lead to plugging in short times. This result is consistent with the recent field experience.[26]

Acknowledgement

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TABLE 1

SOME CHARACTERISTICS OF SUBSTRATES USED

IN COLUMN KINETIC STUDIES

Substrate	Morphology	Surface Area (m^2/g)	Void Vol. (cm^3/g)
Polycrystalline α quartz	Aggregates	3.0	0.47
Monocrystalline α quartz	Single crystal particles	0.03	0.20
Porous Vycor	Amorphous, porous particles	164.	0.70
Powdered Ti metal	Aggregates and single particles	2.4	0.48
Thoria microspheres	Small spheres	0.006	0.088

TABLE 2

COMPARISON OF LEAST SQUARES FITS

FOR SECOND AND THIRD ORDER REACTIONS

Run No.	Column No.	Substrate	pH	Temp. °C	Agreement Factors** 2nd Order (n = 2)	3rd Order (n = 3)
10 OT	1	Polycryst. Qtz.	6.02	60	0.951*	1.038
"	1	"	6.76	"	0.919	0.901*
"	1	"	5.25	"	0.975	0.903*
12 OT	1	"	5.25	"	1.382*	1.487
"	1	"	5.32	80	0.732*	1.161
"	1	"	5.35	100	0.290*	0.893
12 OT	2	"	5.33	100	0.512*	0.957
"	1	"	5.35	60	0.561*	0.636
"	4	Ti Powder	5.34	100	1.00	0.773*
12 OT	3	Polycryst. Qtz.	5.96	60	0.845*	1.588
"	3	"	5.98	60	0.719*	1.654

*The better fit of the two cases tested.

**The agreement factor is the average standard deviation given by

$$\sigma(y) = \left[\frac{\Sigma \, W_i (y_o - y_c)_i}{N_o - N_v} \right]^{1/2}$$

where W_i is the statistical weight, y is the dependent variable, N_o is the number of observations and N_v is the number of independent variables in the calculation.

TABLE 3

COLUMN STUDIES OF DEPOSITION OF SILICA FROM BRINES

Run	Column No.	pH	$[OH^-]^a$ mol/kg	$\frac{m_o}{[SiO_2]}$ mol/kg	A^b cm^2/kg of H$_2$O	Temp. °C	k'^c kg/mol/min	k^d
				Polycrystalline Quartz				
7	1	6.07	2.24E-7	.0085	2.22E+7	60	119. ± 7.8	0.24
	3	6.07	2.24E-7	.0087	2.80E+7	60	195. ± 8.1	0.31
10	1	5.25	3.39E-8	.0088	3.40E+7	60	28.5 ± 2.4	0.14
	2	6.00	1.91E-7	.0088	4.69E+7	60	112. ± 3.7	0.12
	1	6.76	1.05E-6	.0094	3.40E+7^e	60	300. ±19.1	0.14
12	1	5.35	4.27E-8	.0127	0.64E+7	60	7.2 ± 0.2	0.16
	2	5.33	3.63E-7	.0127	1.80E+7	100	94.1 ± 3.5	0.17
	3	5.98	1.82E-7	.0127	0.79E+7	60	42.9 ± 1.0	0.28
13	1	6.00	1.91E-7	.0090	0.95E+7	60	37.2 ± 2.5	0.15
	2	6.00	1.91E-7	.0090	1.18E+7	60	21.1 ± 1.2	0.09
				Porous Vycor				
8	1	6.38	4.6E-7	.0085	94.2E+7	60	51.9 ± 3.7	0.0015
	2	6.69	9.3E-7	.0104	62.5E+7	60	46.5 ± 2.8	0.0012
	3	6.00	1.91E-7	.0126	54.9E+7	60	6.44± 0.28	0.0006
				Monocrystalline Quartz				
10	3	6.77	1.12E-6	.0096	0.11E+7	60	35.1 ± 2.0	0.47
	4	6.00	1.91E-7	.0088	0.074E+7	60	15.6 ± 0.84	1.06
				Titanium Powder				
12	4	5.34	3.72E-7	.0127	1.11E+7	100	40.4 ± 2.8	0.11
13	4	6.00	1.91E-7	.0090	8.19E+6	60	18.9 ± 1.42	0.12
				Thoria Microspheres				
13	3	6.00	1.91E-7	.0090	5.68E+5	60	2.21± 0.47	0.20

^{a}[OH$^-$] calculated from pH measurement and Q_w.

^{b}cm^2 per kg of water in void volume.

^{c}Apparent rate constant – area and [OH$^-$] included.

^{d}Specific rate constant (units omitted because of fractional power of hydroxide concentration).

^{e}This column was subsequently run at pH 5.25, but so little SiO$_2$ was added it was deemed appropriate to use the final area for this run too.