### MATHEMATICAL MODELLING OF SILICA DEPOSITION

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#### Abstract

Various mathematical models describing the rate of depositon of silica from geothermal fluids are investigated. They are combined with the silica transport equation to predict the variation of silica deposition in experimental packed columns and near reinjection wells in geothermal reservoirs.

#### Introduction

One of the major constraints in maximizing the extraction of hot water from liquid dominated geothermal reservoirs is the inevitable deposition of chemicals as exploitation proceeds. Deposition or scaling occurs not only in the bores and surface equipment but also in the reservoir in the immediate vicinity of the wellbore (Cuellar, 1975; Rothbaum et al, 1979; Gudmundsson and Bott, 1979; Weres and Tsao, 1981; Horne, 1982; Itoi et al, 1987a). Silica in amorphous form heads the list of the problem precipitates associated with the reinjection of waste water. Deposition of silica around the wellbore causes reduction in formation permeability, and subsequently the injectivity of the well (Hauksson and Gudmudsson, 1986; Itoi et al,

As the geothermal fluid is extracted and steam is separated considerable supersaturation with respect to amorphous silica results considerable supersaturation with respect to amorphous silica results in the reject water. Amorphous silica deposition may then occur, which appears to be governed by several factors such as degree of supersaturation, temperature, pH, presence of dissolved salts and foreign ions, availability of nucleating species, and fluid flow regime (Henley, 1983). Deposition is known to occur by direct deposition on solid surfaces (heterogeneous nucleation) or by polymerization followed by colloidal deposition (homogeneous nucleation).

Here a mathematical model is developed to describe silica transport in a porous medium which incorporates the changes in porosity and permeability resulting from deposition.

The governing equation is a standard chemical transport equation including a reaction term representing the deposition of silica. The chemical processes involved in silica deposition are complex and the mathematical equations considered here are approximate only. Uncertainty remains on how to best mathematically model silica

Several different forms of mathematical models representing silica deposition are considered here and analytic solutions are obtained for the idealised problem of constant rate injection into either a one-dimensional channel or into a uniform layer from a well, producing radially symmetric flow. The one-dimensional model is also appropriate for analysing experiments on deposition of silica in packed columns.

There are a number of experimental studies made on the kinetics of silica polymerization which have mostly measured the disappearance of monomeric silica during the course of the reaction (Rothbaum and Rohde, 1979; Makrides et al, 1980; Rimstidt and Barnes, 1980; Bohlmann et. al, 1980; Weres et al, 1982; Bird et al, 1986; Fleming, 1986). The kinetics of polymerization are so complex that the studies yielded various estimates of the order of reaction.

Rimstidt and Barnes (1980) performed their experiments in salt-free water and derived from theoretical considerations (Law of Microscopic Reversibility) the kinetics of silica dissolution-precipitation. Their rate equation can be expressed as

$$\frac{dC}{dt} = -k^{-}\frac{A}{M} (C - C_s)$$
 [1]

where k is the precipitation constant, A/M is the ratio of the surface area to the mass of water available, C is the silicic acid concentration (ppm), and  $C_s$  is the saturation concentration. This rate equation characterizes an apparent zero order dissolution and first order precipitation with respect to silicic acid. The rate constant has an Arrhenius temperature dependence.

Bohlmann et al (1980) studied molecular deposition from controlled synthetic solutions. They monitored the deposition of monosilicic acid flowing through a column packed with granular amorphous silica and other similar forms. They found that after the substrate was coated fully with amorphous silica the nature of the substrate had no effect on the rate of deposition. There is little effect of increasing salinity up to 1 molal NaCl and stronger effect at higher concentrations.

Bohlmann et al (1980) fitted their rate data in an empirical form:

$$^{-}$$
=-k'A(C-C) $^{2}$ OH $^{\circ}$ - $^{7}$  [2]

where OH is the hydroxide ion concentration calculated from solution pH, and C is the molal silica concentration. The rate constant k' is independent of temperature over the range 60 to 100°C. The apparent kinetic order for monomeric silica is about 2 and for the hydroxide ion is 0.7.

Rothbaum and Rohde (1979), Makrides et al (1980), and Weres et al (1982) employed nucleation theory to fit their rate data in their polymerization studies, and reported higher reaction orders.

Recently, Fleming (1986) studied silica polymerization (without nucleation) in an attempt to resolve conflicting results on the reaction order. His experiments were performed at 25 - 50°C, 0 -1 molal NaCl and 4 < pH < 8 in unbuffered solutions. Based on the results of his differential rata data, he suggested that there are two different rate limiting regimes, and explained this behaviour by the enhanced solubility, C<sub>x</sub>, of freshly deposited silica. The overall rate of both regimes appear directly proportional to the silica surface area,  $A_s$ . Polymerization is first order in both silicic acid concentration, C, and in the surface concentation of ionized hydroxyl group (surface charge) in amorphous silica, [SiO~].

His model rate equations are for high concentations:

$$\label{eq:forc} \text{forC>C}_x \qquad \qquad \text{[3]}$$
 
$$\boldsymbol{k}_x = \text{k A}_s [\text{SiO}\sim] \qquad \text{and}$$

where

 $k = A_0 \exp \frac{-E}{RT} \exp \frac{A_{DH} \sqrt{I}}{T + \sqrt{I}}$ 

For lower concentration the equation is: 
$$\frac{dC}{dt} = -k_2 (C - C_e)^3 \qquad \text{for } C < C_x$$
 [4]

where

$$\mathbf{k_2} = \mathbf{k_{sr}} \; \mathbf{A_s} \; \Gamma_s^{\; 2} \; \mathbf{C_s}^{-2}$$

and

$$k_{sr}\Gamma_s^2 = A_{sr} \exp \frac{-E_{sr}}{RT}$$
.

The solution pH influences silica surface charge density but not the rate constant, while ionic strength (I) influences both the surface charge and the rate constant k. The complete model was also fitted to the polymerization rate data of Bohlmann et al (1980) and Weres et al (1982), and gave satisfactory results. Malate and O'Sullivan

### **Basic Equations**

The governing equations used in the model represent conservation of mass, momentum, energy and chemicals (Cheng, 1978).

The following general assumptions have been employed:

- Darcy's law adequately describes the fluid movement. The fluid and rock matrix are in local thermal equilibrium.
- The porous medium is homogeneous.

For one-dimensional flow, assuming no sources or sinks, conservation of mass for a single phase fluid can be expressed as:

$$\frac{\partial (\phi \rho_A)}{\partial t} + \frac{\partial Q_m}{\partial x} = 0$$
 [5]

where p^ is the density of the fluid, \$\pp\$ is the porosity of the rock, and Q<sub>m</sub> is the mass flux per unit area. Then Darcy's law gives for horizontal flow

$$Q_{m} = \frac{-k}{v_{4}} \left( \frac{\partial p}{\partial x} \right)$$
 [6]

where v^ is the kinematic viscosity of the fluid and k is the permeability of the rock matrix.

The equation for conservation of energy is

$$\frac{\partial [\phi \rho_{t} c_{t} T + (1 - \phi) \rho_{t} c_{t}]}{\partial t} + \frac{\partial (Q_{m} c_{t} T)}{\partial x} = \frac{\partial}{\partial x} K \begin{pmatrix} \partial T \\ 3\cancel{2} \end{pmatrix} \quad [7]$$

where c<sup>^</sup> is the specific heat of the fluid; p<sub>r</sub>, c<sub>r</sub> are the density and specific heat of the rock matrix, respectively; and K is the thermal conductivity.

Combining equations [5] and [7], and assuming c^, p<sub>r</sub>, c<sub>r</sub>and \$\psi\$ are approximately constant, then the conservation of energy becomes:

$$[\phi \rho_{z} c_{z} + (1-\phi)\rho_{z} c_{z}] \frac{\partial T}{\partial t} + Q_{..m} c \stackrel{\Leftrightarrow}{\wedge} = K \frac{\partial^{2} T}{\partial x^{2}} . [8]$$

The silica mass balance equation can be expressed as

$$\frac{\partial (\phi \rho_z C)}{\int C} + \frac{\partial Q_c}{\partial x} = -R_c \phi \rho_z$$
 [9]

where Q. is the mass flux of silica given by

$$Q_{c} = C Q_{m} - D \frac{\partial C}{\partial x}$$
 [10]

and C is the mass fraction of silica in the fluid and D is the diffusion coefficient. The term R<sub>e</sub> represents the net loss of dissolved silica per unit mass of fluid and is evaluated from one of the kinetic rate equations given above (1,2,3 or 4).

The corresponding differential mass balance for the rock is

$$\frac{\partial [(1-\phi)\rho_{r}Q_{s}]}{\partial t} = R_{e}\phi\rho_{t}$$
 [11]

where Q<sub>s</sub> is the mass fraction of silica in the rock.

For single phase flow which is radially symmetric in a confined layer, mass conservation gives

$$\frac{\partial}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (r Q_m) = 0$$
 [12]

where Q<sub>m</sub> is the radial flux.

Also from Darcy's law,

$$Q_{m} = \frac{-k}{v} \frac{\partial p}{\partial r} . ag{13}$$

And the energy equation is

$$\left[\phi p_{z}c_{z} + (1-\phi)p_{r}c_{r}\right]\frac{\partial T}{\partial t} + \frac{Q_{o}c_{z}}{r}\frac{\partial T}{\partial r} = K\left(\frac{1}{r}\right)\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)$$
[14]

where  $QQ = rQ_m$  is a constant

Conservation of silica is given by

$$\frac{\partial (\phi \rho_{\xi} C)}{at} + \frac{1}{r} \frac{\partial (Q_{\phi} C)}{\partial r} = D \left( \frac{1}{r} \right) \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) - R_{e} \phi \rho_{\xi} [15]$$

The rock mass balance equation is the same as for the one-dimensional flow model.

# Method of Characteristics Solution

In the special case of a constant mass flow, and assuming that diffusion can be neglected in equation [9] then it reduces to a first order partial differential equation of hyperbolic type:

$$\frac{\partial \mathbf{C}}{\partial t} + \mathbf{V} \frac{\partial \mathbf{C}}{\partial x} = -\mathbf{R}_{e}$$
 [16]

Here  $V = Qn/^P$  is the particle velocity and therefore the velocity of movement of chemicals through the porous material.

For this equation it is possible to obtain an exact solution by using the method of characteristics. In particular, characteristic curves are established, along which simple relationships define the transport

By the chain rule, the derivative of C along some curve in the x-t plane can be written as

$$i? = \underline{*}: i1_{+} \underline{*}: ^{L}$$
ds at ds  $3x$  ds [n]

where s is the arc length along the curve.

Comparing equations [16] and [17] the characteristic curves are defined by the following set of ordinary differential equations:

$$\frac{\mathbf{dt}}{\mathbf{ds}} = 1 \quad , \quad -\hat{\mathbf{ds}} = V$$
 [18]

or  $x - Vt = x_0 = constant$  (characteristic line).

Then [16] can be replaced by

$$\frac{dC}{ds} = -R_{\bullet} \quad . \tag{19}$$

The solution of the ordinary differential equation [19] depends now on the form of the reaction term R<sub>e</sub>. As discussed previously (eqns. [1] - [4]) different versions of this form will be considered:

(Rimstidt and Barnes, 1980)

$$\mathbf{R_e} = \mathbf{k}^{-} \frac{\mathbf{A}}{\mathbf{M}} (\mathbf{C} - \mathbf{C_s})$$
 [20a]

(Bohlmann et al, 1980) (ii)

$$R_e = k'' A(C - C_s)^2 OH^{07}$$
 [20b]

(Fleming, 1986) (iii)

$$R_{\textbf{g}} = \begin{cases} kj \ (C - C_x) + k_2 \ (C_x - C / \text{ for } C > C_x \ [20c] \\ k_2 (C - C_s)^3 & \text{for } C < C_x. \end{cases}$$

Note that the original version of Fleming's rate equation was not quite satisfactory and is rewritten here in a modified form to ensure continuity between the two kinetic regimes.

Using Rimstidt and Barnes<sup>1</sup> first order rate equation, equation [19] can be solved along the characteristic line  $x = \hat{V}t + x_0$  in the form

$$\frac{dC}{dt} = -k (C - C_p)$$
 [21]

where 
$$k = k^{-} \frac{A}{M}$$
.

The pertinent initial and boundary conditions are

$$C(x,0) = C_s$$
 [22a]

and

$$C(0,t) = C_0$$
 [22b]

where  $C_o$  is the mass fraction of silica injected and  $C_s$  is the silica saturation concentration.

The solution to this equation is

$$C = C_s + (C_o - C_s)exp - \frac{-kx}{V} \quad \text{for } x < Vt \qquad [23]$$

and

$$\mathbf{C} = \mathbf{C}_{\bullet}$$
 for  $x > Vt$ . [24]

Since [23] is independent of t, it is also the steady state (t  $\longrightarrow$   $\infty$ ) solution.

The two solutions are illustrated in Figure 1. Since V is constant, the characteristics are straight lines. It is clear that the type of solution depends upon the initial point  $(x_o, t_0)$  from which the characteristics emanate. In region I shown by the characteristic AA' (eqn [23]), the characteristic originates from the line x=0, t>0, and in region II shown by the characteristic BB' (eqn. [24]), the characteristic originates from the line t=0, x>0.

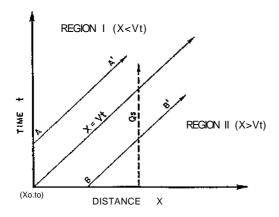


FIG. 1 TIME-DISTANCE DIAGRAM FOR THE SILICA CONCENTRATION.

The rate of silica deposition is evaluated from the rock mass balance equation [11]. Assuming  $p_r$  and ()) are constant, equation [11] becomes

$$\frac{\partial Q_s}{\partial t} = \frac{\phi \rho_t}{(i-\langle i \rangle_0) p_r} \quad k(C-C_s)$$
 [25]

The porosity is given in terms of the amount of silica deposition (Itoi et al, 1987b);

$$\phi = \phi_{o} - \frac{(1 - \phi_{o})\rho_{r} (Q_{s} - Q_{so})}{(1 - \phi_{o})\rho_{o}}$$
[26]

where  $\triangleleft$  and  $p_s$  are the porosity and density of deposited silica, and  $Q_{so}$  is the initial mass fraction of deposited silica in the rock. Substituting eqn. [26] into eqn. [25], and simplifying gives,

$$\frac{\partial Q_s^l}{\partial t} = (\phi_0 - \alpha Q_s^l)\beta(C - C_s)$$
 [27]

where

$$\alpha = \frac{(1-\phi_o)\rho_r}{(1-\phi_s)\rho_s}; \quad \beta = \frac{\rho_s k}{(1-\phi_o)\rho_r} \quad \text{and}$$

$$Q' = Q - Q \quad .$$

Equation [27] can now be easily integrated (see Figure 1) as the two solutions for the silica concentration in regions I and II are both independent of t. The solution is

$$\mathbf{Q}_{c} = \mathbf{Q}_{co} \qquad \qquad \mathbf{x} > \mathbf{V} \mathbf{t} \tag{28}$$

and

$$Q = Q \quad H \stackrel{\phi}{=} 2 \quad \text{II} \quad -exp \quad (f(x,t)) \qquad \qquad x < v t \qquad [29]$$

where

$$f(x,t) = aP(C_o - C_s) exp \left( \begin{bmatrix} kx \\ y \end{bmatrix} \left( \frac{x}{V} - t \right) \right)$$

The solution for C and  $Q_s$  using Bohlmann's and Fleming's rate equation can be determined by following the same procedure. These are summarized as:

### i) Bohlmann et al:

$$C(x,t) = C_{\varsigma} + \left[ \frac{\mathbf{J}}{\mathbf{C}_{\varsigma}} \mathbf{r} \frac{\mathbf{J}}{\mathbf{r}_{\mathbf{C},\mathbf{T}}} + \mathbf{v} \mathbf{v} \right]^{-1}, \mathbf{x} < Vt, \quad [30]$$

where

$$k = k' A OH^{Q7}$$

and

$$C(x,t) = C_s$$
,  $x > Vt$ . [31]

Then [11] can be integrated to give

$$Q_S = Q_{SO} , x > V t$$
 [32]

and

$$Q_s = Q_{so} + \frac{\phi_o}{\alpha} [1 - \exp(f(x,t))]$$
 [33]

where

$$f(x,t) = \alpha\beta \left[ \frac{1}{(c_o - C_g)} + \frac{kx}{V} \right]^{-2} \left( X^{\dagger\dagger} \right]^{1}$$

## (ii) Fleming

For x < Vt

$$C(x,t) = X + (C_0 - X) \exp(-kj x/V), C > C_x [34]$$

and

$$C(x,t) = C_s + \left[ \frac{1}{(C_x - C_s)^2} + \frac{2k}{V} (x - \bar{x}) \right]^{-1/2}, C < C_x.$$
 [35]

where

$$\lambda = C_x - k_2 (C_y - C_o)^3 / k_1$$

and

$$\bar{\mathbf{x}} = \frac{\mathbf{V}}{\mathbf{k}_1} \mathbf{I}_{\mathbf{n}} \left[ \frac{\mathbf{c}_{\alpha'} - \mathbf{x}}{\mathbf{c}_{\mathbf{x}} - \mathbf{\lambda}} \right].$$

Here  $\overline{x}$  is the distance covered when the concentration C falls to  $C_x$ .

For x > Vt  $C = C_s .$  [36]

Then as above  $Q_s$  is obtained by integrating [11]. For x < Vt:

$$Q_{s} = Q_{so} + \oint_{\mathbf{r}} \mathbf{f} \left[ 1 - \exp(f(x,t)) \mathbf{l} \right]$$
 [37]

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where for  $C > C_y$ ,

$$f(x,t) = \alpha \beta (C_o - \lambda) \exp \left(\frac{k_1 x}{V}\right) \left(\frac{x}{V} - t\right)$$
 [38a]

and

$$P = \frac{\rho_k k_1}{(1 - \phi_a)\rho m}$$

ForC<C<sub>4</sub>,:

$$f(x,t) = \alpha \beta^{t} \left[ \frac{1}{(C_{x} - C_{y})^{2}} + \frac{{}^{2} {}^{k} 2}{V} \cdot (x - x)^{-1} \right]^{-3/2}$$
 [38b]

where

$$P^1 = \frac{\rho_4 k_2}{(1-\langle b_0 | pm)} \cdot$$

Similarly for x > Vt

$$Q_s = Q_{so} \cdot$$
 [39]

#### Radial Flow Model

By applying the method of characteristics to the radial flow model, equation [15] is transformed into

where s is the arc length along the characteristic curve

**f-i.** 
$$\frac{d\mathbf{r}}{ds} = \frac{\mathbf{V_r}}{r} .$$
 [41]

Here  $V_r$  is  $rac{dS}{dS}$  are all flow velocity in  $rac{m^2}{
m sec}$ . The characteristic curves obtained by integrating [41] are parabolic:

$$\mathbf{r}^2 - 2V_r t = r_0 2.$$
 [42]

Again the solution obtained by integrating [40] depends on the form of the kinetic equation. The results for the rate equation provided by Rimstidt and Barnes will be presented here. Results for the Bohlmann and Fleming equations can easily be obtained in forms analogous to (30) - (39)

$$C = C_s + (C_o - C_s) \exp \frac{-kr^2}{2V_-}$$
 for  $\hat{r}^2 < 2V_-$ t [43]

and

$$C = C_S forr^2 > 2V_r t. [44]$$

Similarly, the deposition Q<sub>s</sub> is derived for r<sup>2</sup><2V<sub>r</sub>t as

$$\begin{bmatrix}
Q = Q_{so} + \frac{4\pi}{a} \\
1 - \exp\left( ap(C_{o} - C \operatorname{Jexp}\left( \frac{1}{2} - \operatorname{Ising}_{r} \right) \cdot \left( \frac{2}{2V_{r}} - t \right) \right) \\
\text{for } r^{2} < 2V_{r}t
\end{bmatrix}$$

andforr<sup>2</sup>>2V<sub>r</sub>t

$$\mathbf{Q}_{\mathbf{a}} = \mathbf{Q}_{\mathbf{m}} \tag{46}$$

### Model Validation

To test the validity of the equations derived, experimental results obtained by Bohlmann et al (1980) and Itoi et al (1984,1986) were simulated. The experiments were for flow along packed columns so that the one-dimensional flow model is appropriate.

### (i) Bohlmann's Results (see Bohlmann et al, 1980)

The one-dimensional model using their rate equation was first used to match their observed results where outlet silica concentration was measured as a function of residence time in the column. Since their experiments were conducted at steady state conditions and constant temperature, equation [30] was used in the form

$$C = C_s + \left[ \frac{1}{(C_o - C_s)} + kt \right]^{-1}$$
 [47]

where t is the residence time in the column. This is evaluated as

The parameters used in modelling their results are presented in Table 1. Equilibrium concentrations of amorphous silica  $(C_s)$  was calculated from Fournier, (1981).

Table 1. Data Used to Match Bohlmann's Experiments

Column Length	I.D.	<b>C</b> <sub>O</sub> (molal)	pН	$\begin{array}{c} \mathbf{A} & \mathbf{\phi} \\ (\text{cm}^2/\text{kg}) \end{array}$	k <sup>1</sup>
15.2cm	0.84 cm	0.02180	5.25	0.64E07 0.32	0.12
6.0cm	0.95cm	0.00914	6.76	0.90E07 0.30	0.12

Figure 2 shows the good agreement between the observed data and the results predicted by the model despite the fact that there is uncertainty in some parameter values (porosity for example).

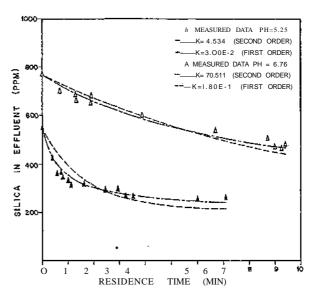


FIG. 2 SILICA CONCENTRATION VS. RESIDENCE TIME.

A first order rate equation (Rimstidt and Barnes, 1980) was also used in the model to match the observed data. The rate constant k—, as derived from Rimstidt and Barnes (1980), was changed since their value is several orders of magnitude less than that required to match the observed data.

The results are also shown in Figure 2. The model using , Bohlmann's rate equation gave a better fit than the first order rate equation.

## (ii) Modelling Itoi's results (see Itoi et al, 1984,1986)

Itoi et al (1984,1986) have also studied amorphous silica deposition in a porous column. In their experiments, a sample of the Otake hot water was introduced at constant temperature into the column packed with aluminium beads. The column was operated at constant pressure and changes in flow rate (due to deposition) were monitored. The amount of silica deposited in the column was then determined after drying the beads.

The result in one of their experiments (Run No. 37) was used to test the applicability of the one-dimensional model in simulating the rate of silica deposition. Here, first and second order rate equations were used, and the flowrate was assumed to be essentially constant throughout the experiment.

Since Itoi et al (1984) did not establish the initial surface area A available for deposition, this term as a first approximation, is represented by (Rimstidt and Barnes 1980);

$$A = \frac{8.55 \text{ V}_{sp}}{r}$$

where  $V_{sp}$  is the specific volume of water in  $m^3/kg$ . This assumes the column consists of closely packed uniform sphere of radius r, and is obviously an upper bound for the simulated conditions. The parameters used in modelling the results of Itoi et al (1986) are listed in Table 2.

Table 2. Data Used to Match Itoi's Experiments

Initial Concentration  $C_o = 475 \text{ ppm}$ Column Temperature  $T = 90^{\circ}\text{C}$ Initial Porosity  $\triangleright = 0.37$ Density of Rock  $p_r = 3300 \text{ kg/m}^3$ Density of Deposited Silica = 2040 kg/m<sup>3</sup> Porosity of Silica = 0.97 Surface Area = 8.86 m<sup>2</sup>/kg Length of Column = 50 cm Diameter of the Column = 5 cm Diameter of the Beads = 2 mm

The initial rate constants calculated from Bohlmann et al and Rimstidt and Barnes did not give the correct initial  $Q_s$ . Hence, several values were tried to match the initial deposition. The simulated results together with the observed data are presented in Figure 3. There is poor agreement between the experimental and model results away from the inlet. The model as shown suggests an almost constant deposition throughout the column.

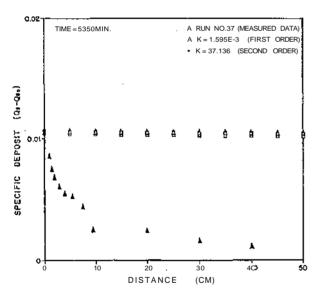


FIG.3 SPECIFIC DEPOSIT VS. DISTANCE.

Matching the distribution of  $Q_s$  proved to be difficult. Once k was selected to match  $Q_s$  at x=0 then no other parameter remains to be selected and the decay away from x=0 depends only on the initial concentration. Itoi and his co-workers also experienced this particular problem (personal communication). In several papers they investigated various alternative reaction models. They found that the only way to match the distribution  $Q_s$  is to use an artificially small initial supersaturation (C-C<sub>s</sub>). Itoi et al (1984) justify this by claiming only some of the silica is available for deposition.

A very low effective initial supersaturation could be explained by polymerization of the monosilicic acid before introduction into the column, or in the early stages of the experiment. The presence of aluminium in Itoi's experiment may have also influenced the rate of polymerization. A small silica concentration decrease at the outlet of the column would support the claim by Itoi et al (1984) that only a small portion of the initial supersaturated silica is available to deposit in the column to form the observed  $Q_{\rm s}$  distribution. However, Itoi does not provide data on concentration measurements at the outlet which could have possibly resolved these conjectures.

### (iii) Results Using Fleming's Rate Equation

Fleming (1986), in his study, suggested two kinetic regimes for silica polymerization. The first regime which is a first order reaction with respect to supersaturation is controlled by the pseudo equilibrium concentation  $C_x$ , expressed in terms of temperature T by

$$1 \text{ n C}_{\mathbf{x}} = 9.74 - \frac{2630}{}$$

where R is the gas constant, 1.987 cal/mole- $^{\circ}$ K. As the monosilicic acid approaches  $C_x$ , a slower reaction follows which he considers as a surface rearrangement reaction of the silica molecule.

The one-dimensional model using Fleming's rate equation was also applied in matching the results of Bohlmann et al (1980) and Itoi et al (1986). Additional data used in modelling the experimental results of Bohlmann et al (1980) are listed in Table 3.

Table 3. Additional Data for Matching Bohlmann's Results

Ionic Strength	pН				$k_{sr}r_{s}^{2}$
M		(nirr <sup>2</sup> )	$(cm^2/cm^3)$	M'V	/ 1 s^A,'1
1.1	5.25	0.0359	6293	13.3	2.06E-5
1.1	6.76	0.3730	8850	13.3	2.06E-5

The silica surface charge [SiO\*] was based on the calculations made by Fleming (1986). The model parameters were slightly varied to match the observed data. The results of the model are presented in Figure 4. Clearly it can be seen that the model and experimental results quantitatively agree especially at lower initial silica concentrations.

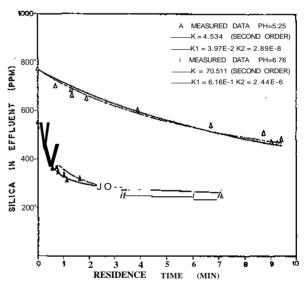


FIG.4 SILICA CONCENTRATION VS. RESIDENCE TIME.

The model was also applied to match the result of Itoi et al (Run No. 37). Again by varying the parameters, the model was able to match the initial  $Q_s$  but did not give the correct profile. Note that the effective supersaturation  $(C_o\text{-}C_x)$  in this case is 32 ppm, which is considerably lower than the previous models (> 100 ppm). However, even this value is not small enough to match the experimental results. There is considerable uncertainty in the calculation of  $C_x$ . To test the effect of varying  $C_x$ , changes were made by varying the temperature.

Since  $C_x$  is a strong function of temperature, an increased temperature increases  $C_x$ . It was increased by pushing up the temperature of the column to  $98.85^{\circ}C$ . This gives the initial "supersaturation" of less than 1 ppm, which is required to match the experimental data.

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The parameters used are listed in Table 4 and the results are presented in Figure 5.

Table 4. Additional Data Used to Match Itoi's Experiment

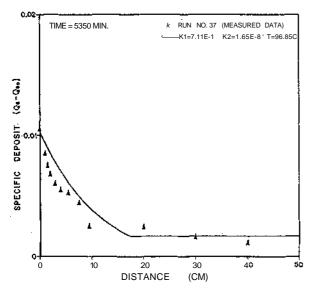


FIG. 5 SPECIFIC DEPOSIT VS. DISTANCE.

Deposition occurs near the inlet of the column which is modelled by the first kinetic regime, and reaches the transition at approximately 18 cm. After the transition, minimal deposition occurs in the part of the column which is modelled by the second kinetic regime.

#### Summary

The method of characteristics has been used to solve the combined silica transport and deposition equation, for several different deposition rate expressions. The most recent deposition rate equation proposed by Fleming (1986) accurately predicts the silica concentration observed in the column studies of Bohlmann et al (1980). Also the experimental studies of Itoi et al (1984, 1986) are explained qualitatively by Fleming's Theory.

The methods considered here can be extended to the non-isothermal case of injection of silica-rich fluid into a reservoir of a different temperature.

### References

- Bird, G., Boon, J. and Stone, T. (1986) Silica Transport During Steam Injection into Oil Sands: I. Dissolution and Precipitation Kinetics of Quartz - New Results and Review of Existing Data. Chem. Geology 54, 69-80.
- Bohlmann, E.G., Mesmer, R.E. and Berlinski, P. (1980) Kinetics of Silica Deposition From Simulated Geothermal Brines. Soc. Pet. Eng. J. 20, 239-248.
- Cheng, P. (1978) Heat transfer in geothermal systems. *Adv. Heat Transfer* 14, 1-105.
- CueJlar, G. (1975) Behavior of silica in geothermal waste waters. In: Proc. 2nd t/JV. Symposium on the Development and Use of Geothermal Resources, San Francisco 2, 1349-1363.
- Fleming, B.A. (1986) Kinetics of Reaction between Silicic Acid and Amorphous Silica Surfaces in NaCl Solutions. J. Colloid Interface Science 110, 40-64.

- Fournier, R.O. (1981) Application of Water Geochemistry to Geothermal Exploration and Reservoir Engineering. *Geothermal Systems*, John Wiley & Sons, 109-143.
- Gudmundsson, J.S. and Bott, T.R. (1979) Deposition of Silica from Geothermal Waters on Heat Transfer Surfaces. *Desalination* 28, 125-145.
- Hauksson, T. and Gudmundsson, J.S. (1986) Silica Deposition during Injection in Svartsengi Field. Trans. Geothermal Resources Council 10, 377-383.
- Henley, R.W. (1983) pH and Silica scaling Control in Geothermal Field Development. *Geothermics* 12,307-321.
- Home, R.N. (1982) Effects of Water Injection Into Fractured Geothermal Reservoirs: A Summary of Experience Worldwide. Fractures in Geothermal Reservoirs, Geothermal Resources Council, Cavis, California.
- Itoi, R. Maekawa, H., Fukuda, M., Jinno, K. Hatanaka, K. Yokoyama, T. and Shimizu, S. (1984) Experimental Study on the Silica Deposition in a Porous Medium. *Trans. Geothermal Resources Council* 8, 301-304.
- Itoi, R., Maekawa, H., Fukuda, M., Jinno, K. Hatanaka, K., Yokoyama, T. and Shimizu, S. (1986) Sudy on Decrease of Reservoir Permeability Due to Deposition of Silica Dissolved in Reinjection Water. *J. Geothermal Res. Soc. Japan*, 8,3, 229-241 (In Japanese).
- Itoi, R., Fukuda, M., Jinno, K., Shimizu, S. and Tomita, T. (1987a) Field Experiments of Injection in the Otake Geothermal Field, Japan. *Trans. Geothermal Resources Council*, 11, 541-454.
- Itoi, R., Fukuda, M., Jinno, K., Shimizu, S. and Tomita, T. (1987b) Numerical Analysis of the Decrease in Injectivity of Wells in the Otake Geothermal Field, Japan. *In: Proc. 9th New Zealand Geothermal Workshop*, 103-108.
- Makrides, A.S., Turner, M. and Slaughter, J. (1980) Condensation of Silica from Supersaturated Silicic Acid Solutions. *J. Colloid Interface Science* 73, 345-367.
- Rimstidt, J.D. and Barnes, H.L. (1980) The kinetics of silica water reactions. *Geochim. Cosmochim. Acta* 44, 1683-1699.
- Rothbaum, H.P. and Rohde, A.G. (1979) Kinetics of Silica Polymerization and Deposition from Dilute Solutions between 5 and 180°C. J. Colloid Interface Science 71, 533-559.
- Rothbaum, H.P., Anderton, B.H., Harrison, R.F., Rohde, A.G. and Slatter, A. (1979) Effect of Silica Polymerization and pH on Geothermal Scaling. *Geothermics* 10, 255-276.
- Weres, O. and Tsao, L. (1981) Chemistry of Silica in Cerro Prieto Brines, *Geothermics* 10, 255-276.
- Weres, D., Yee, A. and Tsao, L. (1982) Equations and Type Curves for predicting the Polymerisation of Amorphous Silica in Geothermal Brines. *Soc. Pet. Eng. J.* 22, 9-16.