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KINETIC EQUATIONS AND TYPE CURVES
FOR PREDICTING THE PRECIPITATION OF
AMORPHOUS SILICA FROM GEOTHERMAL BRINES

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KINETIC EQUATIONS AND TYPE CURVES FOR PREDICTING THE PRECIPITATION OF AMORPHOUS SILICA FROM GEOTHERMAL BRINES

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ABSTRACT

We have experimentally studied the kinetics of amorphous silica precipitation from aqueous solution up to 100°C and containing up to 1M NaCl. Empirical equations for the rate of molecular deposition on surfaces as a function of temperature, dissolved silica concentration, pH and salinity are presented. Empirical type curves which depict the decrease in dissolved silica concentration through homogeneous nucleation of colloidal silica are also presented. Two practical examples related to geothermal practice are given.

INTRODUCTION

It appears that under most conditions silica precipitates as relatively pure amorphous silica. This conclusion is supported by geothermal field experience, laboratory research and theoretical considerations. The scope of our study was restricted accordingly.

The process of amorphous silica precipitation from supersaturated bulk aqueous phase consists of the following steps:

- 1) Growth of polymeric silicic acid complexes to critical nucleus size.
- 2) Nucleation of an amorphous silica phase (from here on simply AS) in the form of colloidal particles.
- 3) Growth of the supercritical AS particles by further molecular deposition of silicic acid on their surfaces.
- 4) Coagulation or flocculation of colloidal particles to give a gel.
- 5) Cementation of the particles in the gel by chemical bonding and further deposition of silica between the particles.
- 6) Rarely, growth of a secondary phase in the

interstices between the AS particles. Such secondary deposition of FeS and of calcite has been reported, but is uncommon.

The above process occurs when the concentration of dissolved silica is high enough for homogeneous nucleation to occur at a significant rate. Very roughly, this requires a saturation ratio (the ratio of concentration to the equilibrium solubility) of two or greater. If this condition is met, massive precipitation occurs. This is the case with the residual (flushed) brine at Niland, Cerro Prieto and Wairakei, and dealing with the consequences presents the greatest technical problems encountered at these sites.

If the concentration of dissolved silica is too low for massive homogeneous nucleation to occur, relatively slow molecular deposition upon solid surfaces becomes the major precipitation mechanism. The product of this process (essentially step 3 of the above scheme alone) is a dense vitreous silica.

The goal of this study has been to generate sufficient experimental data and theoretical analysis concerning steps 1) to 3) to enable their phenomenology and kinetics to be quantitatively predicted and interpreted over most of the range of practical concern.

The results presented in this paper are of a preliminary nature and subject to expansion and revision. We do, however, consider them to be adequate for most practical applications as far as they go.

Values of constants not defined in the text are given in the Nomenclature section.

The Homogeneous Nucleation of Colloidal Amorphous Silica

The voluminous gel-like deposits encountered at Cerro Prieto, Wairakei, and Niland consist of flocculated colloidal amorphous silica. The crumbly grey and white scales associated with the gel-like mater-

ials are cemented colloidal aggregates. This colloidal silica is produced by homogeneous nucleation in the liquid phase, i.e., nucleation by growth of polymers to critical nucleus size without the participation of some preexisting solid particle.

With most substances heterogeneous nucleation is dominant, and homogeneous nucleation is very slow, rare in nature, and difficult to study in the laboratory. The precipitation of amorphous silica is an apparent exception to this because of the very low surface tension of the silica-water interface - between 35 and 50 ergs cm^{-2} over the range of major practical interest. (By comparison, the surface tension of the water-air interface is about 70-80 ergs cm^{-2} .) This means that enormous numbers of particles can be produced by homogeneous nucleation (on the order 10^{17} to 10^{18} per liter), and this completely swamps the effects of heterogeneous nucleation.

We have derived this semi-empirical expression for the surface tension of the AS-water interface:

$$\gamma(\text{ergs cm}^{-2}) = \gamma_0 - n_0 k_B T \ln(1 + K_a S) \quad (1)$$

where

$$\gamma_0 = 59.5 + 0.015 T$$

$$K_a = \exp\left(1.072 - \frac{841}{T}\right)$$

(The second term in (1) expresses the thermodynamic effect of the chemisorption of dissolved silica on the surface of AS.)

A practical consequence of the dominance of homogeneous nucleation is that the precipitation of amorphous silica is experimentally reproducible and predictable. This is because the rate of homogeneous nucleation is determined by basic thermodynamic and chemical variables (concentration, surface tension, etc.) and not by often unknown trace contaminants as is the case with heterogeneous nucleation.

Figures 1 to 4 present experimental results which depict the decline of dissolved silica with time via the homogeneous nucleation mechanism. These experiments were performed at various pH's in a low salinity buffered medium in which the sodium ion activity was approximately 0.069M, and the time scales were shifted to covert all data to a nominal pH of 7.0. These conditions are approximately equivalent to a .088M (= 5200 ppm) NaCl solution at pH 7. Note that the time scales are logarithmic. Thus, at any given temperature, the time needed for homogeneous nucleation to run its course may vary from a few minutes to thousands of minutes, depending on the initial silica concentration.

What is really important here is the saturation ratio:

$$S = C/C_0 \quad (2)$$

to evaluate C_0 , we recommend using the empirical expression given by Fournier and Rowe¹ for the equilibrium solubility of AS:

$$C_0 = \text{antilog}_{10}\left(1.52 - \frac{731}{T}\right) \quad (3)$$

In general, the homogeneous nucleation process is very slow if S is less than about 2.

Note that at the lower initial concentrations at each temperature there is a certain induction period during which there is little concentration change. This is because it takes a certain amount of time for the nucleation process to produce enough particles to noticeably effect the dissolved silica concentration. With higher initial concentrations the induction period is short or even absent due to the much higher nucleation rate. At 30°C and $C_i > 0.7\text{g/L}$, the curves become almost independent of C_i . This is because under these extreme conditions the rate of nucleation proper is so large that it is no longer the rate limiting process.

Practically speaking, with a large initial saturation ratio, amorphous silica gels may form within the process equipment and associated piping. This is observed at Cerro Prieto and Niland. With small saturation ratios, massive precipitation will not occur within the process equipment, but may very well occur further downstream.

We have generated a large quantity of such nucleation data from room temperature to 100°C and have written a computer program which can numerically (and rigorously) model the homogeneous nucleation process; i.e., it can reproduce the curves in these figures. After we have fitted the necessary parameters using our experimental data, we will be able to quantitatively model and predict the process, even under the experimentally inaccessible conditions characteristic of field practice. In particular, Eq.(1) will be adjusted to reconcile it with the nucleation data. The program will be documented and made available to interested outside users.

MOLECULAR DEPOSITION ON SOLID SURFACES

By molecular deposition we mean the formation of compact, nonporous amorphous silica by chemical bonding of dissolved silica molecules directly unto solid surfaces.

Below about 100°C, homogeneous nucleation is usually the dominant precipitation mechanism. The major significance of molecular deposition here is that it is the molecular mechanism of the growth of colloidal particles and of the conversion of gel-like deposits to solid scale. However, at higher temperatures molecular deposition from solution may by itself produce scale at a significant rate. Although the deposition rate is very small (about 1 mm/year in the flashed brine pipes close to the steam separators at Cerro Prieto), this scale is almost indestructible once formed.

We studied the molecular deposition process by adding known amounts of colloidal silica of known specific surface area to our solutions. To calculate the molecular deposition rate per unit area on a spherical particle of radius r , use the expression:

$$R_{md}(\text{g cm}^{-2}\text{min}^{-1}) = k(T)f_{pH}(\text{pH}, [\text{Na}^+]) [1 - S^{-1} \exp\left(\frac{2\gamma}{\rho_n k_B T r}\right)] S^4 \quad (4a)$$

where

$$\log_{10} k(T) = 2.70 - \frac{4102}{T} + (40.0 - \frac{9.8}{T}) \times \frac{10^{-8}}{r} \quad (4b)$$

and γ is to be calculated using Eq. (1). The function f_{pH} accounts for the effects of pH and salinity, and will be presented below. It is equal to unity at $pH = 7$ and $Na^+ = 0.069$. To calculate the molecular deposition rate in the units of $\mu m/day$, multiply the values calculated from Eq. (3) by 6.52×10^6 . The factor in brackets in Eq. (4a) is derivable from the Law of Microscopic Reversibility, and it accounts for the greater solubility of smaller particles. To calculate the deposition rate on a flat surface, set $\frac{1}{r} = 0$.

Note that Eq. (4a) is an apparent fourth order rate law. This shows that the initial formation of the first chemical bond between a molecule of monosilicic acid (MSA) in solution and the silica surface is not the rate determining step of the deposition process. Rather, further condensation and rearrangement of chemisorbed silica species is rate determining. The dependence on S arises because the amount of chemisorbed silica is determined by it. Deposition rates at $pH = 7$, $Na^+ = 0.069M$ and various temperatures and dissolved silica concentrations were calculated (and extrapolated) from our experimental data and are presented in Figure 5. The dashed line represents the approximate concentration limit above which homogeneous nucleation supersedes deposition on added particles as the dominant mechanism. Our data actually covers only the range between 50 and $100^\circ C$ and below the dashed line. However, we believe the extrapolated values to be good enough for practical application.

At any given concentration, there is a temperature at which the deposition rate has a maximum value. Below this temperature, rate increases with temperature in the usual way. Above this temperature, the rate of deposition decreases because the increasing solubility of silica causes the rate of the back reaction (i.e., dissolution) to increase even more rapidly. At the saturation temperature for any given concentration, the deposition rate goes to zero. The practical consequence of this is that the molecular deposition rate is a weak function of temperature at temperatures lower than about $15^\circ C$ below the saturation temperature. However, the rate varies strongly with silica concentration.

EFFECTS OF pH

It has long been believed that the rate of amorphous silica deposition is proportional to the surface density of ionized silanol groups on the silica surface². Our experiments on the pH dependence of the rate proved this hypothesis conclusively. We found that the rate as a function of pH calculated from our data matched surface charge vs. pH data in the literature³ to within experimental error.

The function f_{pH} fitted to our data and evaluated at $[Na^+] = 0.069$ is presented in Figure 6. It is the solution of an equation which describes the exchange of protons on the silica surfaces for sodium ions. Unfortunately, there is no closed form expression for f_{pH} . In order to facilitate numerical use of f_{pH} , We have fitted empirical closed form

expressions to the "exact" calculated values. These are given below for a constant sodium activity of 0.069M.

At $pH < 5.9$, use the expression:

$$\log_{10} f_{pH} = x - 2.2583f_0 + \log_{10}(1-f_0) + 0.9248 \quad (5a)$$

where

$$x = pH - 7.6$$

$$f_0 = \text{antilog}_{10} x$$

At $5.9 < pH < 8.0$, use

$$\log_{10} f_{pH} = x - 2.113 \log_{10} (1 + \text{antilog}_{10} (x/2.113)) - x/(9.6538 + 1.7901x + 4.1811x^2) + 0.9248 \quad (5b)$$

We found that the reaction rate ceases to increase in proportion to surface charge at about pH 8. This is due to the offsetting effect of the increase of silica solubility with increasing pH. Our data suggests that for $8.0 < pH < 9.0$ it is an adequate approximation to set $f_{pH} = 2.70$. Our results should not be used about pH9.

Increasing the pH at constant salinity increases the rates of molecular deposition and homogeneous nucleation by the same factor. The effect upon the latter is a consequence of the effect upon the former.

EFFECTS OF SALINITY

Dissolved salts have two important effects upon these processes:

- 1) They decrease the solubility of amorphous silica and, thereby, increase the rate of homogeneous nucleation.
- 2) Increasing the salt concentration at constant pH increases the surface charge density and, thereby, the rate of molecular deposition.

The second effect increases the rates of molecular deposition and homogeneous nucleation by the same factor. The first effect increases only the rate of homogeneous nucleation. It will be discussed in detail below.

Except at very low salinity, most of the dissociated silanols on the silica surface have cations bound to them - in the case of our experiments, sodium. This means that sodium and hydrogen ion activity do not have independent effects upon the rate; rather, it is the ratio of sodium to hydrogen activity that is important. Therefore, Figure 6 and the expressions for f_{pH} given above may be used to calculate the effect of salinity upon the molecular deposition rate as well.

To do this, calculate a "nominal pH value" defined by

$$pH_{nom} = pH + \log \frac{[Na^+]}{0.069} \quad (6)$$

and then read off the value of f_{pH} from Figure 6 or

calculate it from Eq. (5a or b) using the value of pH_{nom} in place of pH.

For example, to calculate the molecular deposition rate of 100°C, pH 6.5, $[Na^+] = 0.069M$ and 0.7g/L dissolved silica: First, read the deposition rate at pH 7.0 and $[Na^+] = 0.069M$ from the Figure 5. This value is 0.22 $\mu m/day$. Second, calculate pH_{nom} using the equation above. This is 7.5. Third, read the value of f_{pH} (7.5) from Figure 6; this is 1.8. Finally, multiply the two numbers together to obtain the deposition rate which is 0.40 $\mu m/day$.

Our data suggests that this procedure is adequate for solutions which contain up to at least 1M NaCl, and it may be adequate at even higher salinities. However, it cannot be recommended for use at salinities much below 5200 ppm. At very low salinities dissociation without ion pairing becomes important, and the basic assumption of the equivalent and opposite effects of hydrogen and sodium activity collapses. We hope to remedy this shortcoming by detailed reanalysis of the low salinity surface charge data in the literature.

The dissolved solids in real geothermal brines are usually predominantly sodium chloride, but other salts are also present. We have found that, in most cases, it is sufficient to use an "effective sodium ion activity" calculated as 0.77 times the (molar) concentration of chloride. If bicarbonate is present as a major ion, use the sum of the chloride and bicarbonate concentrations in place of chloride alone. The rationale for this procedure is that the various other major cations that may be present have essentially the same effects as sodium, and the activity lowering effects of divalent anions approximately compensates for the concentration of the cations that accompany them.

We have studied homogeneous nucleation in NaCl solutions both experimentally and theoretically, and have managed to quantify the "solubility effect" ((1) above) as well. To within experimental error, we are able to account for it using the simple artifice of a "nominal concentration":

$$C_{nom} = C [1 + 0.057 M_{NaCl}] \quad (7)$$

The value of C_{nom} is to be used in place of C only in connection with Figures 1 to 4. Do not use it in connection with Figure 5 or Eqs. (2) and (4a).

Thus, to approximately predict the course of homogeneous nucleation for a given set of conditions:

- 1) Calculate C_{nom} and look up or interpolate the appropriate curve in Figures 1 to 4.
- 2) Calculate pH_{nom} and f_{pH} (pH_{nom}) using Eq. (5a or b) or Figure 6.
- 3) Shift the time scale of the curve obtained in step 1) by $\log_{10} f_{pH}$ in the appropriate direction.

We have also studied the catalytic effects of fluoride. This data has not yet been completely

analyzed. However, practically speaking, the effect of 20 ppm fluoride may be ignored above about pH 5, and that of 2 ppm fluoride may be ignored above about pH 4.

SOME PRACTICAL EXAMPLES; OR, HOW NOT TO REINJECT

Case 1):

Consider a hypothetical geothermal development at which the spent brine contains 5200 ppm NaCl, 0.5 g/L dissolved SiO_2 , and is delivered to the reinjection well at 75°C and pH 7. The brine delivered to the reinjection well is completely clear and goes right through a membrane filter. The decision is made to reinject. Reinjection commences at 400 t/hr into an aquifer of 200°C initial temperature, $\phi = 0.1$, $h = 20$ m and volumetric solid rock heat capacity = 2460 $kJ/m^3 \cdot ^\circ C$. After about 12 days the thermal front is about 60 meters into the formation, and the fluid travel time from wellbore to thermal front is about 50 hours = 3,000 minutes. Referring to Figure 2, we see that there is now ample time for homogeneous nucleation to occur before the fluid reaches the thermal front. The result is that the injectability of that horizon is damaged by silica precipitation. Furthermore, well treatments with caustic or HF are not effective because the damage is 30 to 60 meters away from the wellbore.

Case 2):

Can one reinject straight from the first stage steam separators at Cerro Prieto? Assume the following typical brine conditions at the injection well: 160°C, 0.95 g/L dissolved SiO_2 , effective $[Na^+] = 0.25$ and negligible suspended solids. The brine pH at reservoir temperature is not known, but is approximately 7.8 at room temperature. This gives a nominal pH of about 8.3 (which is within the range of weak pH dependence) and $f_{pH} = 2.7$ (from Figure 6). The $pH_{nom} = 7.0$ deposition rate is read from Figure 5 as about 1.3 $\mu m/day$. Correcting for pH, we obtain the actual deposition rate of 3.5 $\mu m/day = 1.3$ mm/year. This is consistent with the observed rate of vitreous silica deposition near the separators at Cerro Prieto. Because pore permeability is dominant at Cerro Prieto, it is clear that injecting this brine would rapidly plug the injection well.

We hope that such mistakes will be avoided. However, we emphasize that both of these brine streams would be deemed injectible under the criteria presently in vogue: they would be able to pass freely through a micron-sized membrane filter and would not cause visible fouling of metal surfaces during field tests of a few days duration. It is precisely the refinement of such criteria that we hope to have accomplished with the work summarized here.

NOMENCLATURE

All concentration in this paper are expressed in terms of g/L or moles/L. What is meant is the amount of material that would be contained in one liter of brine cooled down to room temperature. Therefore, these concentration values do not vary with temperature, and are equal to concentrations

in terms of amount per Kg H₂O at low salinity. This convention was chosen because it is most convenient for laboratory work and seems to be the one usually employed in geothermal practice.

AS abbreviation for amorphous silica

C = concentration of dissolved silica in g SiO₂/L (referred to room temperature; see above)

C_i = initial concentration of dissolved silica; g/L

C_{nom} = "nominal concentration" of dissolved silica (see text)

C₀ = concentration of dissolved silica in equilibrium with solid AS at a given T and low salinity; g/Kg H₂O

f_{pH} = function which expresses the effect of pH and salinity upon the rate of molecular deposition (see text); dimensionless

k_B = 1.38054×10^{-16} ergs K⁻¹; Boltzmann's constant, a fundamental physical constant

k(T) = the apparent rate constant for molecular deposition at pH = 7 and [Na⁺] = 0.069

K_a = the equilibrium constant for chemisorption of dissolved silica on the surface of AS; dimensionless

M_{NaCl} = concentration of sodium chloride; moles/L

[Na⁺] = sodium ion activity

n₀ = 8.14×10^{14} cm⁻² = the surface density of sites for chemisorption on the surface of AS (a theoretical estimate)

pH = minus log base 10 of the hydrogen ion activity

pH_{nom} = "nominal pH" (see text)

r = the radius of a spherical particle of AS; cm

R_{md} = the rate of molecular deposition of dissolved silica on an AS surface; g cm⁻² min⁻¹

S = C/C₀ = saturation ratio; dimensionless

T = absolute temperature; Kelvins

γ = surface tension of the AS-water interface; ergs cm⁻²

γ₀ = surface tension of the AS-water interface in the hypothetical state of no chemisorption; ergs cm⁻²

n = 10^{22} cm⁻³ = the number density of SiO₂ units in solid AS

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FIG. 1 - HOMOGENEOUS NUCLEATION AT 100°C. $pH=7.0$, $Na^+=0.069M$; I.E., $pH_{NOM}=7.0$. CURVES LABELED WITH VALUES OF $C_i\ (g\ L^{-1})$. NO DISCRETE DATA POINTS BECAUSE DATA GENERATED BY A CONTINUOUS FLOW SYSTEM.

FIG. 2 - HOMOGENEOUS NUCLEATION AT 75°C, $pH_{NOM}=7.0$. DISCRETE DATA POINTS GENERATED BY PERIODIC MANUAL SAMPLING.

FIG. 3 - HOMOGENEOUS NUCLEATION AT 50°C, $pH_{NOM}=7.0$

FIG. 4 - HOMOGENEOUS NUCLEATION AT 30°C FOR $C_i \geq 0.7$, 23°C FOR $C_i \leq 0.6$. $pH_{NOM} = 7.0$

FIG. 5 - RATE OF MOLECULAR DEPOSITION OF SILICA ON A FLAT AS SURFACE AS A FUNCTION OF TEMPERATURE AND CONCENTRATION

FIG. 6 - RATE OF MOLECULAR DEPOSITION RELATIVE TO THE RATE AT $pH_{NOM} = 7.0$; I.E., $F_{PH}(pH_{NOM})$.