PREDICTING THE PRECIPITATION OF
AMORPHOUS SILICA FROM GEOTHERMAL BRINES

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I. 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 materials 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.

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.

Figure 1 shows some typical 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 convert 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 scale in Figure 1 is logarithmic. With an initial concentration of 1.1g/liter of SiO_2, the reaction runs most of the way to completion in less than 10 minutes.* With an initial concentration of 0.5g/liter, it takes about 5,000 minutes. In

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*Here and elsewhere in this paper, concentrations are expressed in terms of grams or moles/liter referred to room temperature. Therefore, we mean that this solution would contain 1.1g/l SiO_2 if cooled to room temperature, but not necessarily at 75°C.

other words, 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 (0.5g/l corresponds to S=1.9 at this temperature), massive precipitation will not occur within the process equipment, but just as certainly will occur somewhere further downstream. Also note that 0.5 and 0.7g/l curves show an induction period during which the concentration does not change noticeably.

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 Fig. 1. 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. This program will be documented and made available to interested outside users.

II. 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 onto 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. Deposition rates at pH 7, $[Na^+] = 0.069$ and various temperatures and dissolved silica concentrations were calculated (and extrapolated) from our experimental data and are presented in Figure *2.* 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°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, the 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°C below the saturation temperature. However, the rate varies strongly with silica concentration. (Our data is best fitted by an apparent fourth order rate law.)

111. Effects of pH and Salinity

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 surface. 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 literature to within experimental error.

The rate as a function of pH for $[Na^+]$ = 0.069 is presented in Figure 3. The function plotted in Figure 3 is the rate at any given pH relative to the rate at pH 7. 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.

We found that the reaction rate ceases to increase in proportion to surface change at about pH 8. This is due to the offsetting effect of the increase of silica solubility with increasing pH. Our data suggest that a constant pH correction factor of about 2.7 is adequate between about pH 8 and 9. The results presented here should not be used above pH 9.

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 elsewhere.

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 3 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

$$\text{pH nom} = \text{pH} + \log \frac{[Na^+]}{0.069}$$

and then read off the pH correction factor from Figure 3 using the nominal pH value instead of the real one.

For example, to calculate the molecular deposition rate at 100°C, pH 6.5, $[Na^+]$ = 0.69M and 0.7g/l dissolved silica:

First, read the deposition rate at pH7.0 and $[Na^+]$ = 0.069M from Figure 2. This value is 0.22 µm/day. Second, calculate pH nom using the equation above. This is 7.5. Third, read the pH correction factor for pH 7.5 from

Figure 3; this is 1.8. Finally, multiply the two numbers together to obtain the deposition rate which is 0.40 µm/day.

Our data suggest 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 compensate for the concentration of the cations that accompany them.

IV. Some Practical Examples; or, How Not to Reinject

Case 1):

Consider a hypothetical geothermal development at which the spent brine contains 5200 ppm NaCl, 0.5g/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 400t/hr into an aquifer of 200°C initial temperature, $\phi=0.1$, $h=20$ m and volumetric solid rock heat capacity = $2460 kj/m^3$ 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 hour = 3,000 minutes. Referring to Figure 1, 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 injection 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 a pH factor of 2.7 (from Fig. 3). The pH nom = 7.0 deposition rate is read from Fig. 2 as about 1.3µm/day. Correcting for pH, we obtain the actual deposition rate of 3.5µm/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.

Acknowledgements

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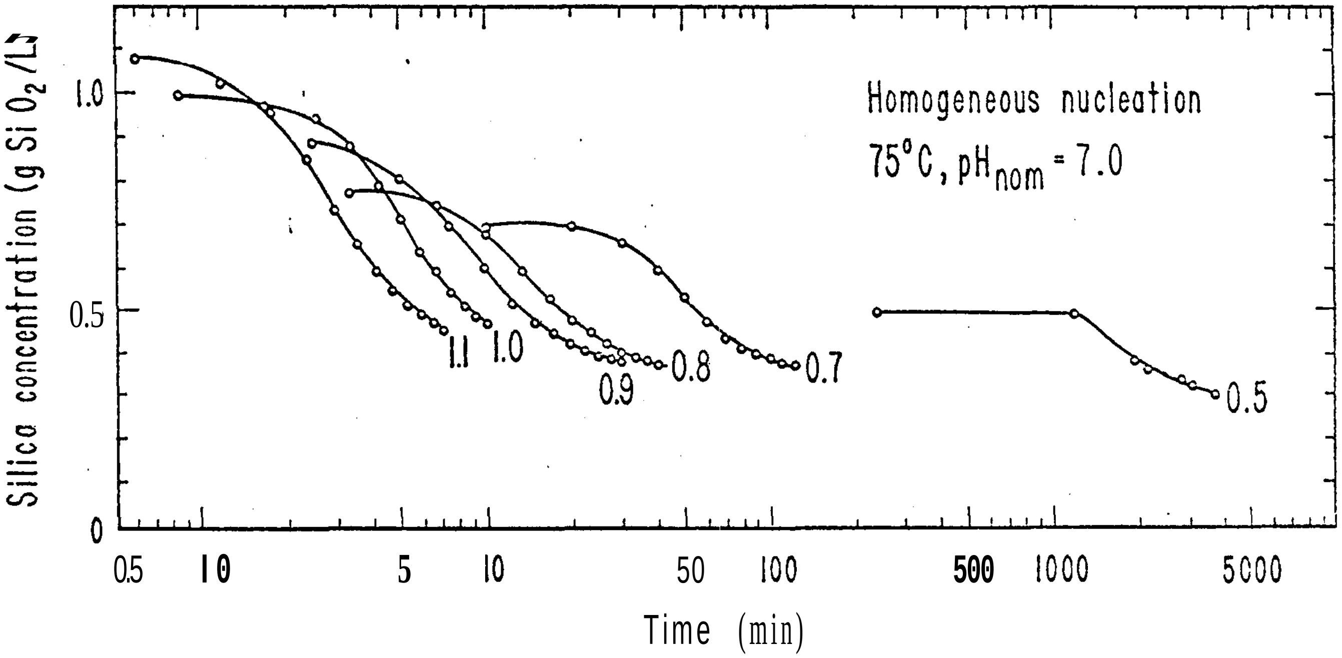

Figure 1. Decrease of dissolved silica concentration with time under conditions of homogeneous nucleation at 75°C, pH 7.0 and sodium activity = 0.069M. Numbers on Figure indicate initial dissolved silica concentrations.

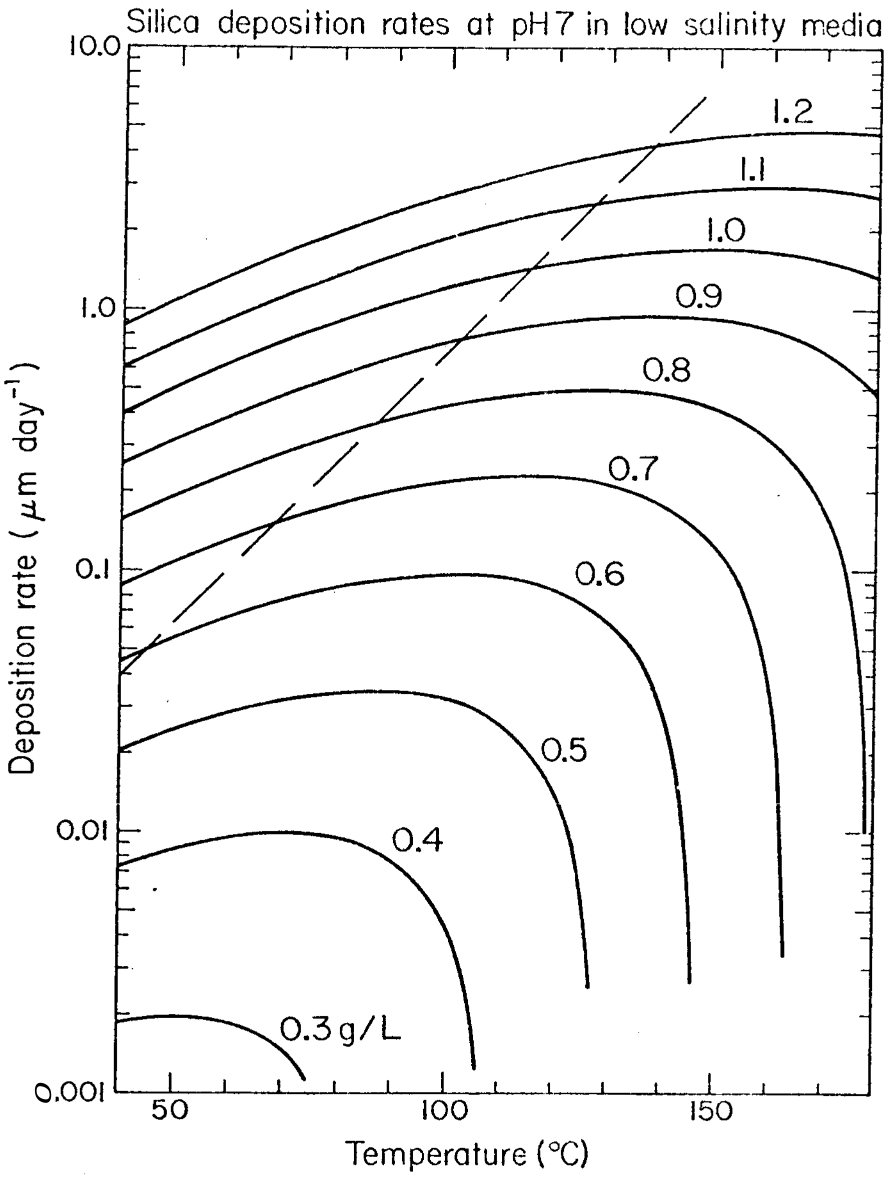

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Figure 2. Rates of molecular deposition of silica upon a flat surface at pH 7.0 and sodium activity = 0.069M. Dissolved silica concentrations corresponding to each curve indicated in g/liter referred to room temperature.

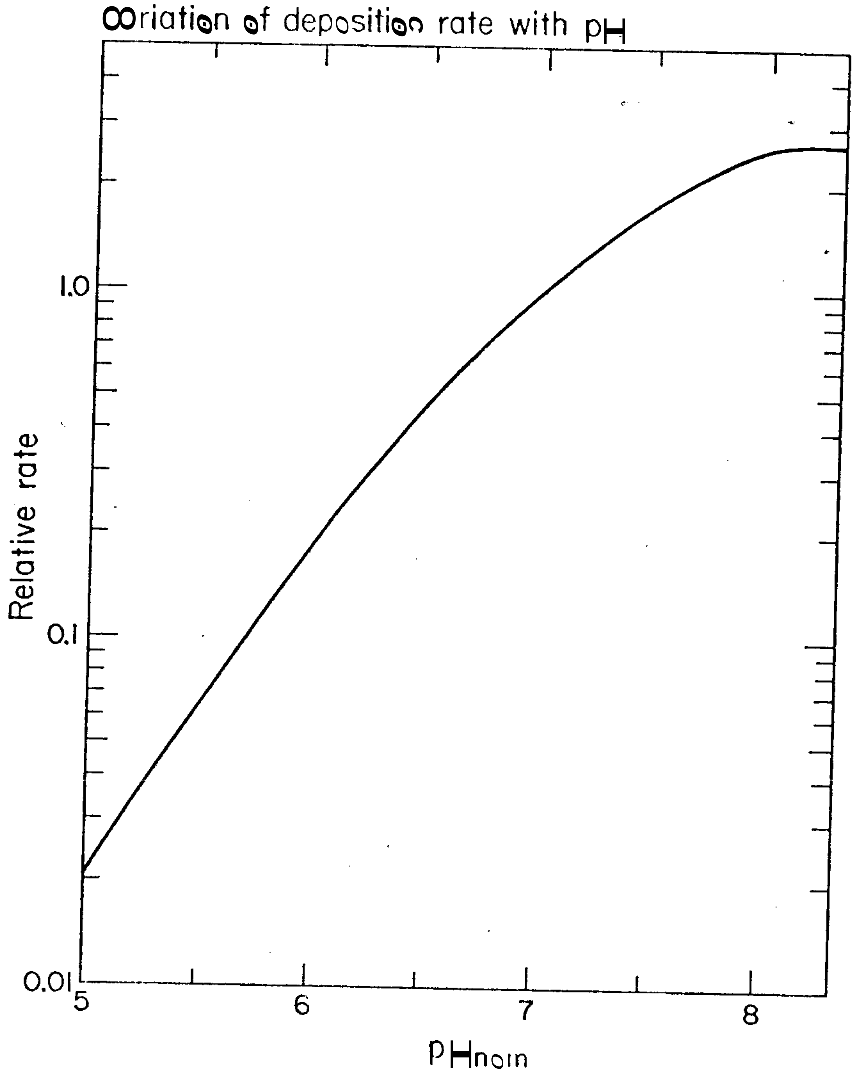

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Figure 3. Variation of molecular deposition rate with pH_{nom}. Curve gives the rate as a function of pH_{nom} relative to the rate at pH_{nom} = 7.0. At pH_{nom} greater than 8, use the value 2.7 for the pH correction factor. When sodium activity = 0.069M, pH_{nom} = pH.