CONTROL OF SILICA SCALING

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Both the equilibrium chemistry of silica solubility and kinetics of the dominant reactions suggest methods of preventing scale formation in the development of hot water-dominated geothermal resources.

At equilibrium, the dominant solubility-fixing reaction is

$$SiO_2(s) + 2H_2O \rightarrow 4H_4SiO_4(aq.)$$

for pH's less than 9, - the usual condition. Starting with a geothermal solution of a specific silica concentration, precipitation may be initiated by decreasing temperature (Fig. 1) or water purity (Fig. 2). The stoichiometry of this reaction shows that the solubility is a function of

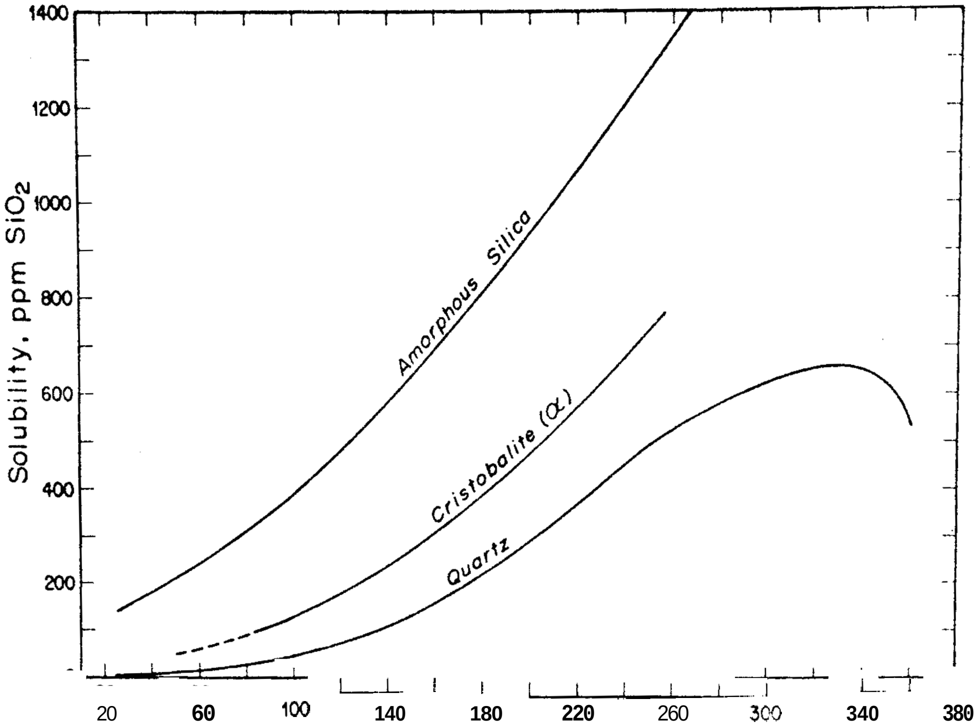

Fig. 1. Solubility of silica phases in water. (Data from references 1, 2, 3, 4, 5, 6, 8, 9, and 11.)

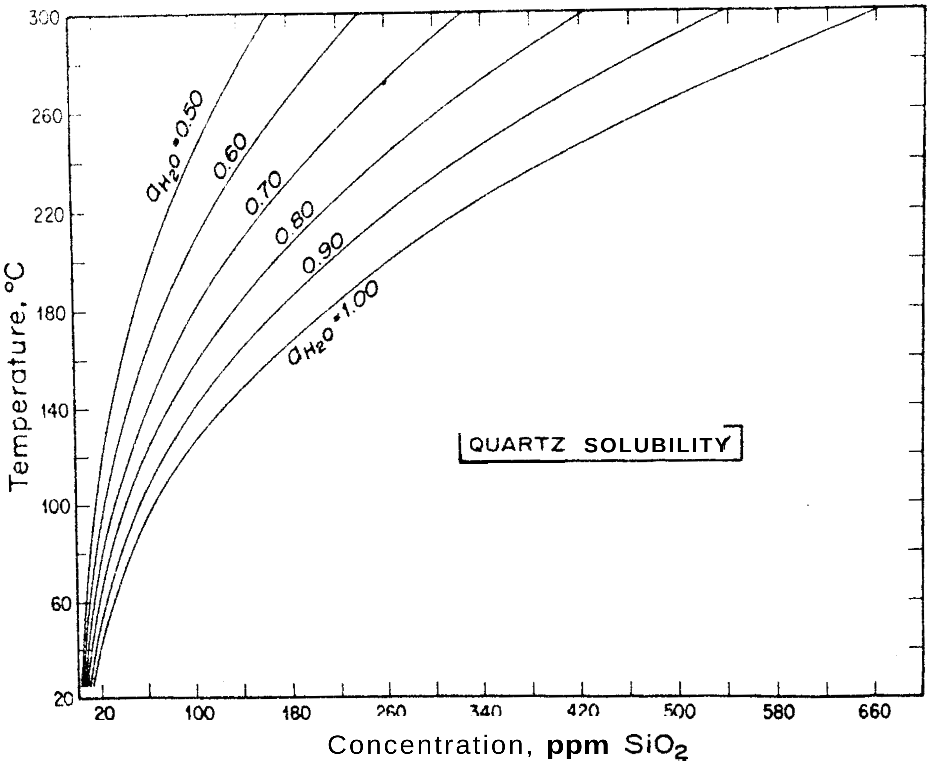

Fig. 2. Quartz solubility at various temperatures and activities of water. The activity of water varies with salt concentrations typically as follows:

~~Concentrations~~

a_{H_2O}	NaCl m	NaCl %		CaCl$_2$ m	CaCl$_2$ %
0.90	2.8	14		**1.6**	15
0.75	6.2	27	(sat. at 25°C)	-	
0.70	-			3.4	22
0.50	-			5.0	36
0.30	-		(sat. at 25°C)	7.2	44

These values are exact for temperatures near 25°C and approximately correct to 350°C.

water activity, $a^2_{H_2O}$ as demonstrated by the linearity of the curve on Fig. 3, so that an increase in ionic strength, due to evaporation (flashing) or to dissolving of salts, greatly reduces solubility. Consequently, equilibrium relations show that precipitation can be delayed by: (1) maintaining the temperature of the solution close to that of the geothermal reservoir for as long as possible prior to heat extraction, and (2) by dilution. In appropriate circumstances, favorable dilution can be

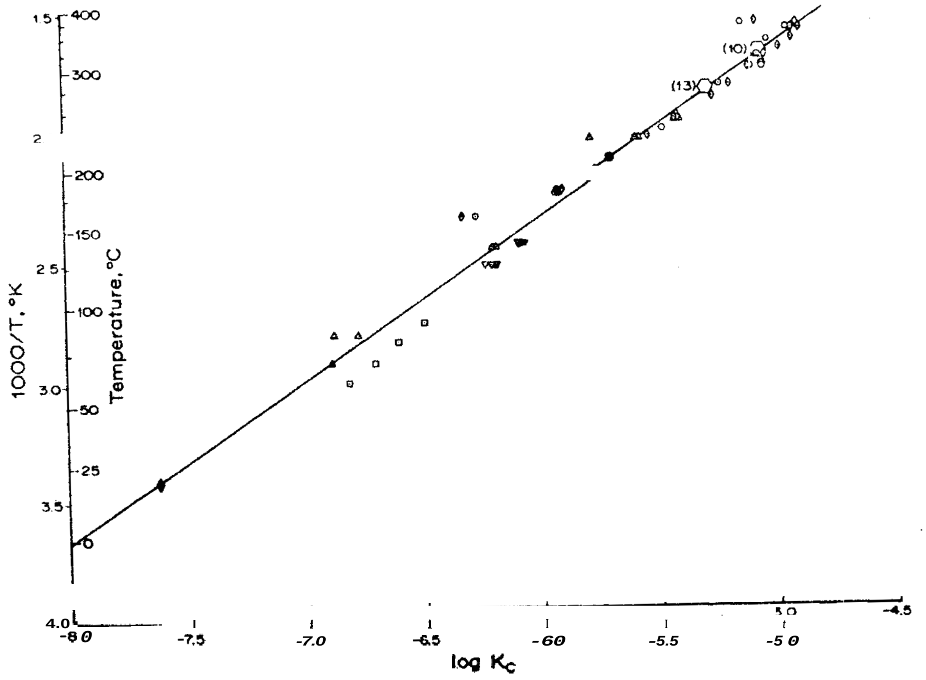

Fig. 3. The complete equilibrium constant for quartz solubility where $K_c = \frac{aH_4SiO_4}{aSiO_2\ (H_2O, g/cc)^2}$.

(Solubility data from references 1, 4, 5, 6, 8, 9, and 11.)

realized by mixing the output from one well with that from a second with either lower salinity or silica content. Another process causing dilution is to use a steam-driven, downhole pump. Because flashed steam is always relatively pure compared to the residual solution, if this steam is injected to power the pump, the effluent also effectively dilutes both the initial silica content and the salinity, a dual bonus.

Kinetic effects are at least equally promising for controlling silica deposition. The rate of precipitation at temperature, T, is

$$\left(\frac{\partial(SiO_2)}{\partial t}\right)_T = K_p(H_4SiO_4)(S/V)$$

where K_p is the rate constant and (S/V) is the surface area on which deposition is taking place per unit volume of solution[10]. Clearly, the surface area (and roughness) in geothermal systems should be minimized to slow rates of deposition. Alternatively where supersaturation is inevitable, silica can be scrubbed from the solution by countercurrent flow of fine-grained, inert solids (with high surface area) to nucleate and remove the excess silica.

Because K_p is exponentially dependent on temperature, the solution should not be allowed to cool slowly from high temperatures (Fig, 4). If saturation is reached at high temperatures, precipitation is fast due to the high rate of reaction. However, if the solution is cooled abruptly, the silica is quenched into solution and can only precipitate very slowly at low temperature. Consequently, single-stage heat extraction minimizes scale formation. Sufficient rate data have not as yet been accumulated to quantify this method, unfortunately.

Silica polymerization seems not to be important to the kinetics of geothermal systems. Rates are probably significant only at high alkalinities at high temperatures and at pH 8-10 at low temperatures[3]. Furthermore, analyses of geothermal fluids by the monomer-detecting molybdate technique also appears to give reliable values for the total silica concentration present.

The severity of scale formation apparently also depends in part on salinity. Highly saline solutions, such as those from the Salton Sea KGRA, readily deposit massive scale while less saline solutions, as at Cerro Prieto, may not precipitate more than minor amounts before rejection.

	T	(Cl^-)		(SiO_2)
	°C	m	ppm	ppm
Salton Sea	320	3.1	155,000	400
Cerro Prieto	350	0.2	10,000	500

As suggested by several authors, this effect may be caused by catalysis of precipitation reactions by chloride concentrations above roughly 0.01 m[10]. At higher Cl^- concentrations, there is also the untested possibility that silica-chloride complexes form. Dilution of such brines is especially effective in retarding scale deposition. In addition to lowering the initial silica concentration and raising the ultimate solubility by increasing a_{H_2O}, the rate of deposition is lowered by decreasing the concentration of this catalyst. Again, considerable data are needed to determine the exact concentration ranges where catalysis and complexing become important. These values are being obtained as functions of time, temperature, and chloride concentrations using the experimental system shown on Fig. 5.

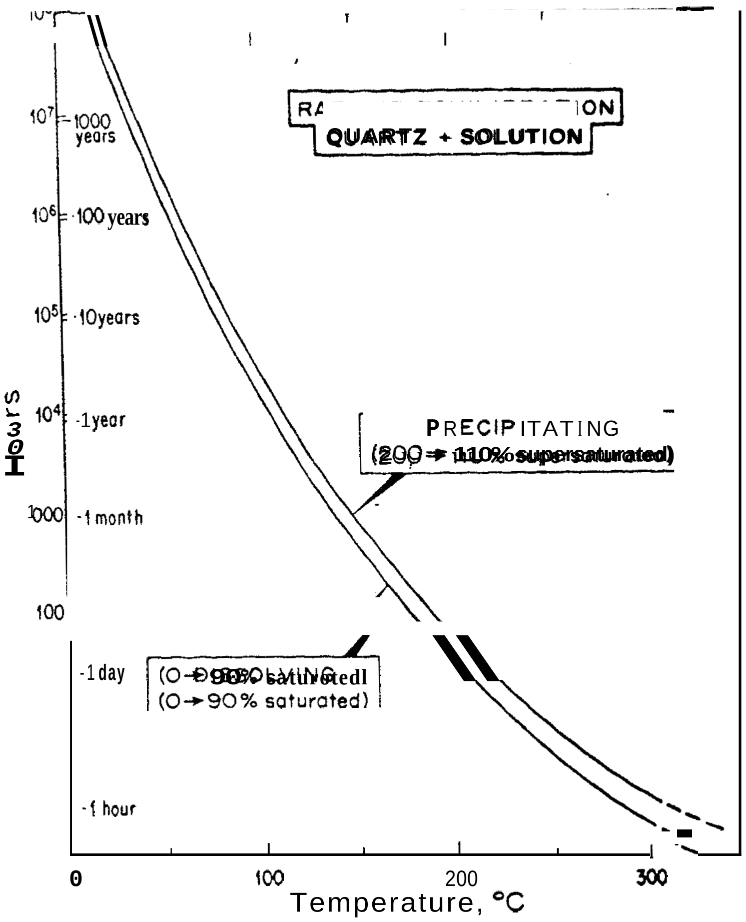

Fig. 4. Preliminary curves showing the rates of dissolving and precipitating of quartz as a function of temperature. Dissolving - Amount of time necessary for water in a geothermal reservoir to become 90% saturated with H_4SiO_4 if the ratio of the silica surface area to the volume of solution is 14.9 cm^2/ml (equivalent in the reservoir to 1 ml of solution within a fracture of 1 in2 area). Precipitating - Amount of time necessary for water in a pipe which contains twice the saturation concentration of H_4SiO_4 to precipitate enough quartz to reach 110% of saturation if the pipe has a ratio of surface area to volume of solution of *6.6* cm2/ml (~800 ft2/gal).

These rates will be faster for cristobalite and amorphous silica in direct proportion to their higher a_{SiO_2} and also higher due to any catalysis, for example by F^- of Cl^-.

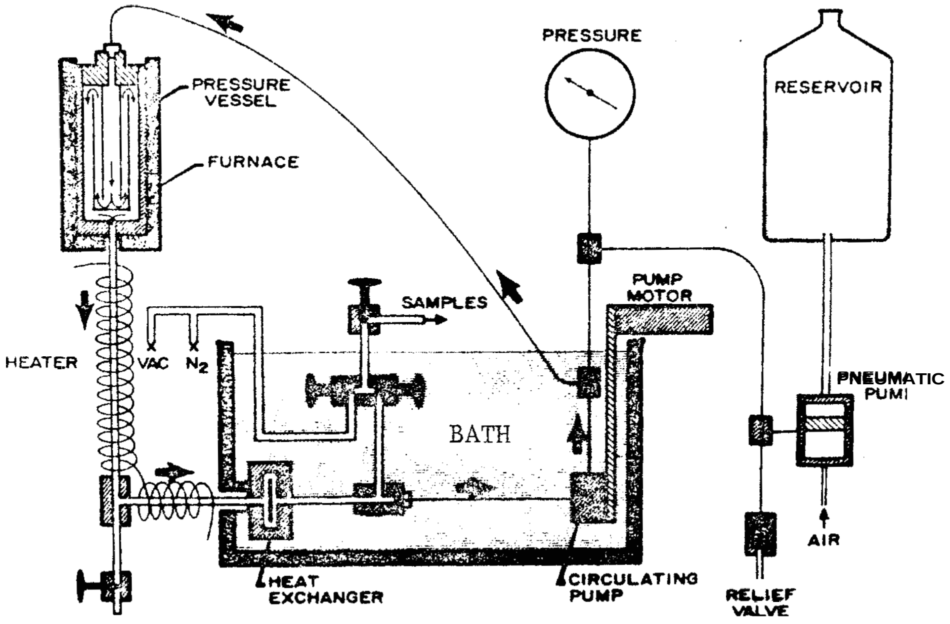

Fig. 5. Experimental system for determining reaction rates. In the 1 liter pressure vessel, either well characterized rock or mineral samples are held in circulating solutions at temperatures up to 450°C and pressures to 3500 p.s.i. Analyses of periodic samples of solution and of deposits in the heat exchanger, plus evaluation of alteration of the rock samples, permits determination of the principal reactions and the derivation of their rate constants.

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