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PREDICTION AND PREVENTION OF SILICA SCALING AT LOW LEVELS OF OVERSATURATION: CASE STUDIES, AND CALCULATIONS FOR UENOTAI GEOTHERMAL FIELD, AKITA PREFECTURE, JAPAN

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ABSTRACT

Production system design studies often include site-specific silica scaling field experiments, conducted because the onset and rate of scaling are believed difficult to predict, particularly at relatively low levels of oversaturation such as may exist in separators, flowlines, and injection wells. However, observed scaling occurrences (Cerro Prieto, Dixie Valley, Svartsengi, Otake, Hatchobaru, Milos, experimental work) actually conform fairly well to existing theory and rate equations. It should be possible to predict low level scaling with sufficient confidence for production and injection system design and, in cases where oversaturation is allowed, to design systems with foresight to suppress or manage the scale which develops. A promising suppression technology is fluid pH reduction by mixing with non-condensible gases and/or condensate. Calculations for injection lines at Uenotai geothermal field indicate molecular deposition at rates of 0.1 to 1 mm/yr, and some potential for particle deposition at points of turbulence, which can be suppressed by an order of magnitude with about 500 ppm CO_2. Further improvements of predictive technique will benefit from more uniformity in designing experiments, reporting results. and reporting measurements of scaling in actual production systems.

INTRODUCTION

In spite of the phenomenal industry success in learning to manage the severe silica scaling from hypersaline geothermal brine at the Salton Sea in California, scale development from low levels of oversaturation in more typical, lower salinity waters remains a nuisance. The pressure/temperature at which a boiling wellflow saturates with amorphous silica often is used to constrain the design of production conditions. When oversaturation is allowed, typical scale management includes periodic clean-out or replacement of separators and pressurized disposal lines, and allowing the fluid to flash to atmospheric pressure so that silica can be driven out of solution and removed by chemical/mechanical means (e.g., flocculation and settling) before the residual brine is injected back into the reservoir. Where the oversaturation of pressurized brine is not too severe, direct injection may be practiced. However, silica scale is often the inferred cause of mild to severe permeability losses in injection wells.

Because silica scaling mechanisms are fairly complex and poorly quantified, it has been common to design scale management on the basis of local field experiments. From our experience with published and unpublished studies, comparison of results has been hindered by a lack of uniformity in experimental design, methodology and reporting.

In this context, a study was undertaken to assist production - injection system design at Akita Geothermal Energy Company's Uenotai Field (Menzies and others, 1990; Robertson-Tait and others,1990). The purpose of this work was to review existing theory and case studies, produce a model of expected fluid behavior and scaling, and make design recommendations.

It was assumed that steam separation would occur at 8.1 or 9.3 bar (170 or 175°C), and that maximum injection pipeline residence times would be 20 to 45 minutes during 30 years of production. The residence times were calculated from production simulations and preliminary pipeline designs. Averaged fluid samples from two similar wells were considered. Table 1 provides an example. A correction was made for the slightly different average pressures of the water and gas samples. Note that the Uenotai water is quite dilute, in spite of high reservoir temperature (c.280°C at well T-51).

SCALING MECHANISMS

When reservoir water boils and loses steam through a pressure drop silica saturation can be simply calculated using a graphical solution (figure 1). The figure shows the solubilities of quartz (Fournier and Potter, 1982), chalcedony (determinations by Fournier, 1981 and Arnorsson and others, 1983), and amorphous silica (Fournier, 1981; Chen and Marshall, 1982; Fournier and Marshall, 1983), all plotted at steam saturation enthalpy. A straight line passes through two known

Table 1 : Averaged Sample Data, Well T-51

Total flow enthalpy 447.98 cal/gm

Water fraction:
Separation pressure 5.0 bar
(9 to 17 samples each parameter)

Parameter	mg/l	Parameter	mg/l
Ca	0.39	Tot.Alk(as HCO_3)	56.08
Mg	0.04	SO_4	31.24
Na	180.50	Cl	247.56
K	37.14	SiO_2	892.27
Li	0.55	F	2.34
Cs	0.03	B	1.24
NH_4	0.42	H_2S	11.76
Al	1.38		
As	0.24	pH (lab.)	8.89/22°C

TDS(meas.)	1,374.06	Ion balance	
TDS(sum)	1,418.69	(difference/sum)	+1.29
TDS_m/TDS_s	0.969		

Gas fraction:
Separation pressure 4.5 bar
(9 to 11 samples each parameter)

Dry gas	CO_2	83.98 vol.%
	H_2S	6.48
	N_2	4.06
	CH_4	5.66
	H_2	4.94
Gas/steam		2,727. mm/1.000m

points (steam at separation pressure and the reservoir) and leads to the silica concentration in the residual liquid. The case shown is the wellhead at Uenotai well T-51 during a 3 month flow test in 1988, when there was 340 mg/kg oversaturation with amorphous silica, and a thick deposit of soft white scale formed on the control valve (wellhead conditions 4 bar/142°C).

A complete review of silica chemistry with respect to oversaturation response is beyond the scope of this paper, but a summary of the most essential and satisfactory theory is needed. Major bibliographies are provided by Marsh and others (1975), Iler (1979) and Chan (1989).

The dissolved silica usually reported as SiO_2 behaves in solution as a molecule named silicic acid, written as $Si(OH)_4^o$ or $H_4SiO_4^o$. This can be described as a combination of SiO_2 with two water molecules. More essential is the concept that it contains four separate -OH groups bonded to a central Si atom. In turn, these "silinol" groups have two essential behaviors.

One behavior is acidity. A silinol group can loose its proton (H^+), although silicic acid is weak and therefore insignificantly ionized at low pH. The loss of one proton produces silicate ion:

$$H_4SiO_4^o = H_3SiO_4^- + H^+.$$

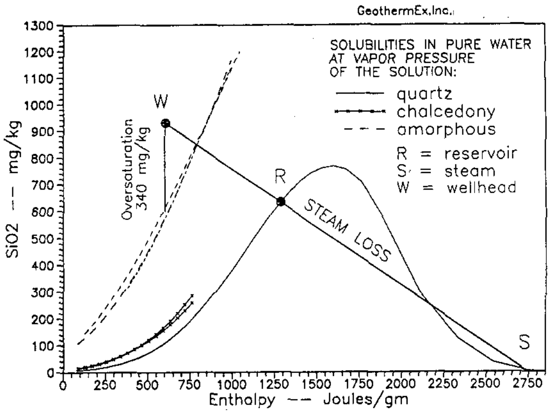

Figure 1. Silica versus enthalpy during boiling.

The proportion of silicate ion to unionized silica ($H_3SiO_4^-/H_4SiO_4^o$) is about 1/100 at pH 7.8 (25°C), rising to 1/1 at pH 9.8 (25°C). From 25°C to about 175°-200°C the acidity increases by about an order of magnitude (1/1 ratio at about pH 8.8); then it decreases again as temperature rises further. $H_2SiO_4^=$, which forms when a second proton is lost, remains nearly insignificant except at very high pH. Some $H_3SiO_4^-$ is conventionally considered to combine with Na^+ to form dissolved sodium silicate, $NaH_3SiO_4^o$.

The second behavior is reactions between silinol groups to form the Si-O-Si bonds in silica minerals. These reactions determine the maximum undissociated $H_4SiO_4^o$ in a solution at a given temperature. Solution composition also has an effect, whereas pressure has little effect unless extremely high.

Reservoir water at thermodynamic equilibrium typically contains $H_4SiO_4^o$ in a concentration determined by the least-soluble solid phase, pure SiO_2 as quartz. Below about 180°C, quartz tends to develop in a particular form called chalcedony, which has somewhat higher solubility (figure 1). When a quartz-saturated solution oversaturates by boiling, it rarely forms quartz scale unless temperature remains above about 220°C, because the rate of crystal growth is extremely slow relative to wellbore processes.

In such cases, a boiling/cooling solution can eventually oversaturate to the point where $H_4SiO_4^o$ becomes limited by Si-O-Si bonding into polymers. The initial step in this process is a "condensation reaction", between two silicic acid molecules:

$$H_4SiO_4^o + H_3SiO_4^- = H_6Si_2O_7^o + OH^-.$$

Deposition onto a solid surface begins by an analogous process, where dissolved silicic acid reacts with an -OH group on a corroded iron.

Compared to quartz crystals, the growing polymers are messy, with irregular surfaces, numerous remaining silinol groups, and infinitely branching structures.

However, they equilibrate with a predictable concentration of low molecular weight silicic acids; this concentration defines the solubility of amorphous silica (figure 1). It is common to refer to this solubility as the concentration of monomeric silica (also termed m-SiO_2) or $H_4SiO_4^\circ$; this terminology is used herein. In actuality, the soluble silica is a mixture of low molecular weight silicic acids (monomer, dimer, trimer; Marsh and others, 1975).

In all cases of solubility (quartz, chalcedony, amorphous silica), any ionized silica present exists in addition to $H_4SiO_4^\circ$. As a consequence, the apparent solubility given by total SiO_2 in solution (T-SiO_2 = unionized SiO_2 + ionized SiO_2) increases as pH increases. Figures 2 and 3 show the difference between total SiO_2 and SiO_2 in $H_4SiO_4^\circ$ calculated for the Uenotai fluid, plotted versus pressure and then temperature instead of enthalpy. The relevant calculations are described in Appendix A.

pH also exerts significant control on polymerization rate. The causes of this are not completely understood, but implied by the condensation reaction as written above. Polymers grow by collision of an unionized -OH unit on one molecule with an ionized $-O^-$ on another, releasing OH^- into solution (Marsh and others, 1975). This indicates that polymerization rates should be at a maximum when the concentrations of available -OH and $-O^-$ on growth surfaces are equal. In a slightly oversaturated solution, this is the pH at which $H_4SiO_4^\circ = H_3SiO_4^-$ (pH 9.8 at 25°C; 8.8 at 175°-200°C, see above). Large polymers have higher acidity, so a strongly oversaturated solution can exhibit its maximum growth rate at somewhat lower pH.

The pH effect generally is observed, and as an approximate rule lowering pH slows kinetics by a factor of about 10 for every pH unit (e.g. Rothbaum and others, 1979; Hirowatari and Yamaguchi, 1990).

In an oversaturated solution, the relationship between polymer growth and actual scale deposition is a function of combined chemical and physical processes which follow two dominant and essentially competing pathways: molecular deposition and particle deposition.

Molecular deposition occurs when the growing polymer surface is a solid, to which silicic acid and silicate ions migrate by circulation and diffusion. The rate of deposition is a function of temperature, supersaturation, and the density of silinol groups ionized to $-Si-O^-$ on the solid growth surface. The effective surface density increases with salinity and, of course, pH (Weres and others, 1982). This rate is discussed further below.

Particle deposition follows nucleation and growth of suspended polymers. The starting process is termed homogeneous nucleation because the polymers develop spontaneously in solution and not by deposition onto foreign particles or ions of other solutes. This is a chemically reversible process. It starts with an "induction period" which rolls smoothly, on a logarithmic time scale, into a period of rapid polymer growth, then slowing growth as the oversaturation of the solution is depleted. At low levels of oversaturation (and/or low pH) the induction period can last minutes to hours. When initial supersaturation exceeds about 2 to 2.5, the induction period often is instantaneous, and polymer growth very rapid.

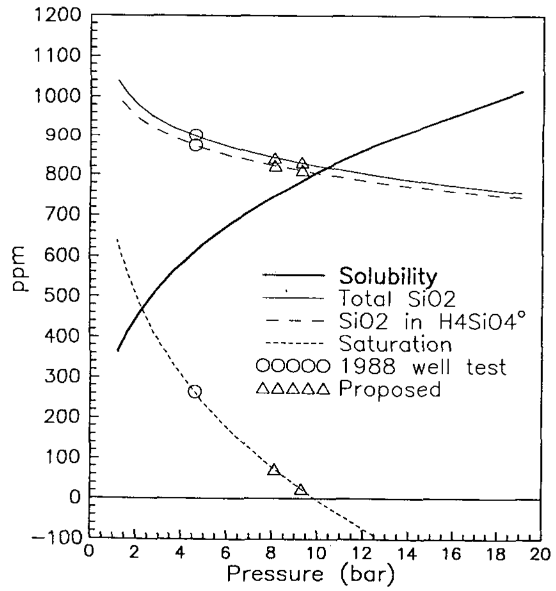

Figure 2. Silica versus pressure, Uenotai well T-51.

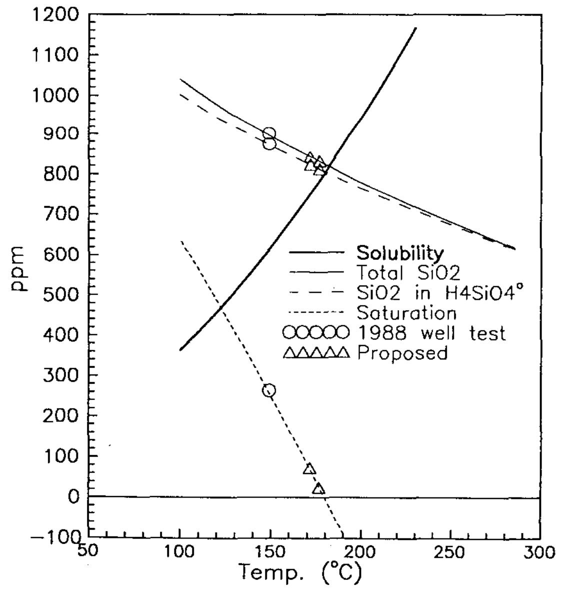

Figure 3. Silica versus temperature, Uenotai well T-51.

Many studies of induction period and polymerization rate have been published (e.g., see Kindle and others, 1974; Hurtado and Mercado, 1990; and Thordarson and Tomasson, 1989). However, it must be considered that such studies typically are context specific, depending strongly on SiO_2 concentration, temperature, salinity and pH. Induction will be shorter at higher SiO_2; for a given SiO_2 level induction will be shorter at lower temperature, higher salinity, and higher pH, except when counteracted at very high pH by increased solubility. Marsh and others (1975) also note that many studies of polymerization rate have been flawed by inadequate experimental technique and misinterpretation of results. Weres and others (1982) have discussed a computer program for calculation of nucleation rates (see below).

The properties of the growing polymers, such as individual size and acidity, change continuously as they grow, and different solutions mature differently. For example, the relatively low nucleation rates at high temperatures cause formation of fewer particles which tend eventually to become larger. At low temperature there typically is a higher supersaturation ratio, and nucleation produces larger numbers of smaller particles. High pH causes rapid growth of many particles which aggregate quickly into larger units, whereas low pH promotes the continued separate growth of smaller particles.

There is a loosely defined size (usually termed "critical size") above which the growing polymers are considered to be colloidal particles. At this point they are spherical in shape, and once greater than about 10 nm in diameter, they apparently grow by molecular deposition at the same rate as surface scale. There is competition between surface scale and suspended particles for the supply of excess $Si(OH)_4$ in solution. Therefore, when the particles are abundant and growing, the rate of molecular deposition onto solid surfaces (e.g., pipe walls) may decrease, because the particles are taking $Si(OH)_4$ out of solution.

The colloidal particles can deposit as scale when they reach solid surfaces, driven by diffusion, flow turbulence, and sometimes gravity. If these transfer processes are rapid, scale can grow on the surface much more rapidly than it could by molecular deposition alone. Mass transfer tends to be most rapid at low temperature, when particle sizes are small, and at high turbulence. Adhesion of particles onto solid surfaces appears to be both a chemical and a physical process; once adhered, the particles can become cemented by further molecular deposition. In static or slowly flowing regimes, the scaling process can be affected further by coagulation or flocculation of colloidal particles to give either a precipitate or a suspended semi-solid material, or a gel; some solutions form stable colloids which do not precipitate.

Molecular deposition is primarily responsible for producing hard, vitreous, often dark colored scale, with density about 2.1 to 2.3 g/cc. In contrast, particle deposition produces white, fluffy, scale with dry density about 0.95 g/cc. Exceptions to these rules have been described, including hard scale believed to have deposited by particle deposition, and soft white scale which formed at low oversaturation within the expected induction period (Jamieson, 1984). Changes in flow rates or supersaturation may be marked by alternating laminae of vitreous and fluffy scale. In pipelines, the scale often forms radial ridges transverse to the flowpath, which can cause considerable roughness to fluid flow (e.g., Stock, 1990).

SCALING EXPERIENCE

Several recent reports of scaling experience were considered in light of the processes above. Available descriptions are typically incomplete (see recommendations below), but most allow an illustration of scaling rate or effects in relation to temperature or pressure and SiO_2 concentration.

Cerro Prieto, Mexico: Scaling in a pilot facility and in disposal lines (figure 4) has been described by Hurtado and Mercado (1990). The pilot plant data represent fluid from one well processed at a rate of 9.1 t/hr through two or three stages of steam separation. Scaling in the plant was highly concentrated at points of turbulence, and figure 4 shows what appear to have been the maximum scaling rates. The scale was not described, but probably formed by particle deposition.

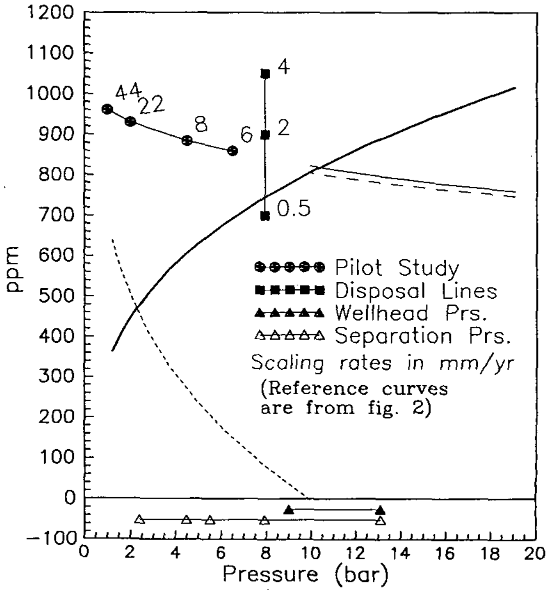

Figure 4. Silica versus pressure, showing scaling rates, Cerro Prieto.

The disposal line data represent maximum rates at 7 wells flowing for 6 years at 170°C. The rates of 0.5 and 4 mm/yr were measured in single flow lines, and SiO_2 for the point at 0.5 mm/yr probably has been underreported. The point at 2 mm/yr is the rough average of 1 mm/yr to 3 mm/yr at 5 wells with SiO_2 between 800 and 1000 ppm. Scale morphologies were not described.

Figure 4 also shows the range of wellhead pressures and steam separation pressures currently in use at Cerro Prieto. Most wellhead pressures are above the point of silica saturation, but steam separation pressures are low enough to allow scaling to occur.

Dixie Valley, Nevada (chemical data courtesy of Oxbow Geothermal Corp., W.R. Benoit, private communication): The reservoir water at Dixie Valley is almost as dilute as at Uenotai, although temperature is lower and alkalinity is higher, so that pH at a given temperature is higher by about 0.5. Cl in injection lines is 395 mg/l. Figure 5 shows total SiO_2 in high pressure separators and at injection wellheads, and unionized SiO_2 at injection wellheads. We calculate that pH at the injection temperature of 106°C is 8.3, so there is a large difference between total SiO_2 and unionized SiO_2. Data from Stock (1990) indicate that injection line residence times vary from 27 to 58 minutes, with most injection wells 30 minutes downstream from a production separator.

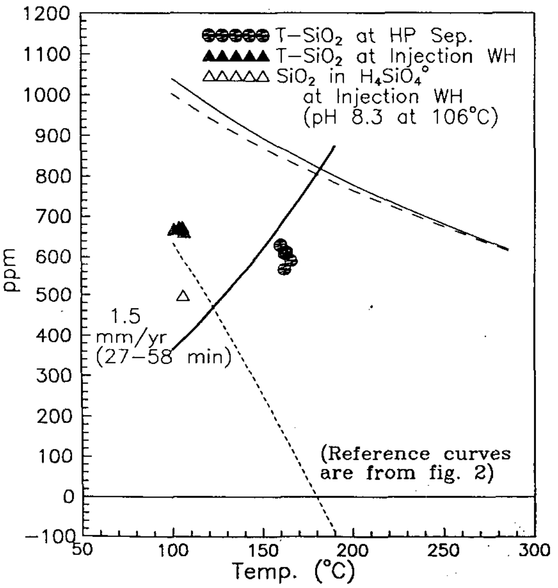

Figure 5. Silica versus temperature at Dixie Valley, with injection line scaling rate.

In straight runs of the injection line, thin silica scale was deposited in 2 to 3 mm high radial sawtooth ridges which faced upstream (Stock, 1990). The duration of flow was not reported but probably was 1 to 2 years; hence the average 1.5 mm/yr on figure 5. In one elbow, the scale was as thick as 6.5 to 13 mm, and consisted of thin flakes oriented almost perpendicular to the pipe walls in an extreme form of the sawtooth ridge pattern. Generally the surface of the scale could be easily scraped to a smooth base, and no hard glass scale was seen. Particle deposition is indicated, and explained by rapid nucleation at very high pH.

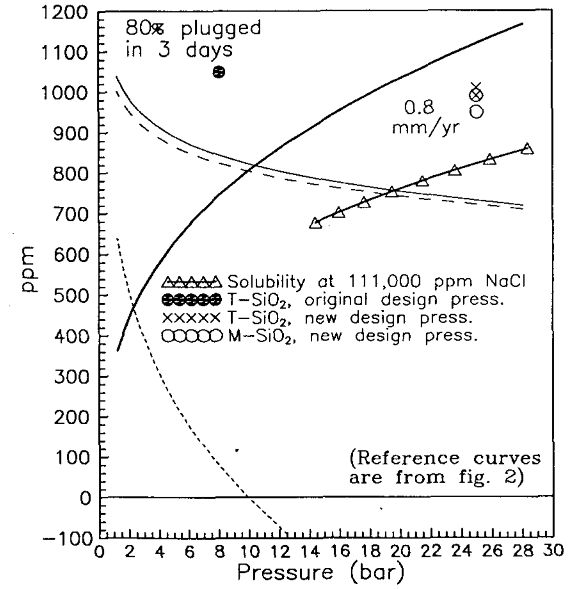

Figure 6. Silica versus pressure at Milos, Greece, with injection line scaling rate.

Milos, Greece: The water contains about 65,000 ppm Cl, so the high salinity requires recalculation of amorphous silica solubility (figure 6). When this water was produced at the original design pressure 8 bar abs., there was extreme scale deposition (Hibara and others, 1989; Karabelas and others, 1989). To manage this, the production system was re-designed to separate steam and water at 25 bar abs. The brine was then pumped under pressure about 1 km to an injection well. In this new system, metal sulfides deposited in the 2 phase line and separator, iron-enriched amorphous silica scale deposited along much of the length of the injection line, and about 0.8 mm/yr of nearly pure silica scale deposited on the pipeline walls and on coupons near the injection wellhead. The injection well showed no damage after six months. There were several system outages during the 3 months of coupon test flow; Hibara and others (1989) believe that cooling during these periods may have caused some of the measured 0.8 mm/yr scale formation.

Hibara and others (1989) described the coupon scale only as "layers with voids between", whereas Karabelas and others (1989) used "a clearly opaline substance" to describe another scale sample from about the same point. A micrograph showed that this substance consisted mainly of flaky grains with diameter about 1-10 μm, also with a few large grains of sulfides in a siliceous matrix. The sulfide was likely carried in from upstream. The morphology suggests particle deposition cemented by considerable molecular deposition. Hibara and others (1989) measured the SiO_2 in the 25 bar brine and reported that there was less than 50 ppm oversaturation. Our own calculation of solubility indicates closer to 100 ppm oversaturation.

Otake and Hatchobaru, Japan: At Otake (figure 7) a cooled mix of production waters from atmospheric flash was injected for two years into two wells at 80°C, 60°C and 50°C (Itoi and others, 1989). Total SiO_2 was measured in the mix after cooling to 95°C, and total and monomeric SiO_2 were measured in samples collected from downhole in the two injection wells. Figure 7 shows only the 95°C mix and concentrations in the 80°C water. There was a considerable loss of injectivity, especially at 60°C and 50°C, and caliper logs and televiewer logs showed scale in the injection well casings and liner slots.

At Hatchobaru (Hirowatari and Yamaguchi, 1990) a continuous flow of brine cooled to various temperatures was mixed in a pilot apparatus with gas extracted from the power station (70% CO_2). Scale deposition was measured after 24 to 72 hours of flow. The unaltered brine had pH about 7.5 and average SiO_2 850 mg/l, and apparently it formed scale at 0.4 to 1.6 mm/yr, although the data are sketchy and the morphology of the scale was not described. In contrast, gas-treated brine at 59°C with pH 5.3 formed scale at only 0.01 mm/yr (converted from mg/day assuming density 2.2).

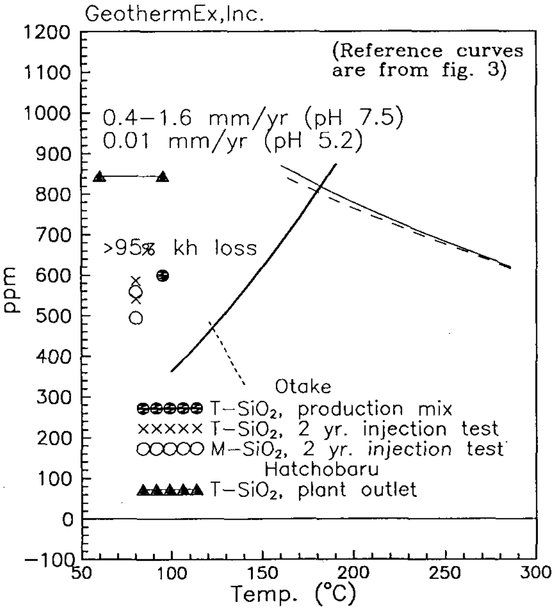

Figure 7. Silica versus temperature at Otake and Hatchobaru, with scaling data.

Svartsengi, Iceland: The brine here is two-thirds seawater. Thordarsson and Tomasson (1989) report that after vacuum separation at 0.3 bar/70°C, the brine pH is 7.9 and there is strong scaling; therefore, surface disposal is used. Brine with 550 ppm total SiO_2 has been used for studies of pH and temperature effect on polymerization. In 1984, this brine was mixed with condensate and gases to lower the pH, in order to inhibit scaling and allow a long-term injection test (Hauksson and Gudmundsson, 1986). The mixture pH was 6.4 to 6.8, and it was oversaturated by about 200 mg/l. Scaling rates from the mixture after 13 to 22 days of flow were 2.8 to 3.0 mm/yr downstream of injection line pumps, 4.6 to 6.6 mm/yr on the front of an orifice at the injection wellhead, and 0.04 mm/yr on the back of the same orifice. Residence time was c.15 minutes. Particle deposition is indicated.

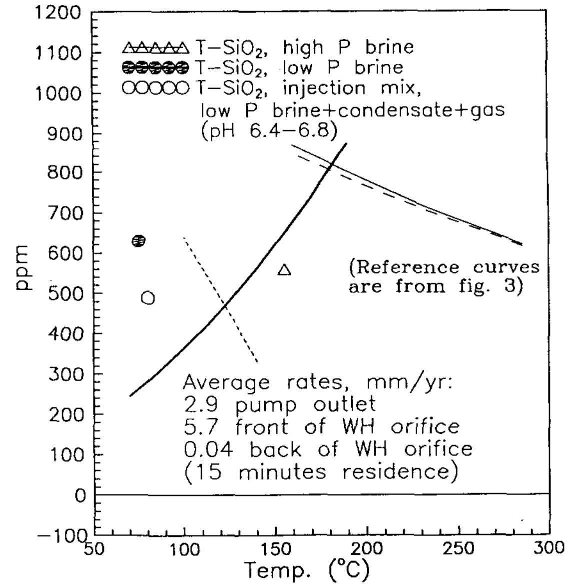

Figure 8. Silica versus temperature at Svartsengi, with injection line scaling rate.

Mroczek and McDowell (1990): This well-controlled and documented experimental work was conducted by passing separated brine from a well through a pipeline for 29 to 35 days. Then the pipeline was cut into even sections and the amount of scale in each section determined. Eight experiments were run, two each with separator pressure set for 180°C, 160°C, 140°C and 120°C. At each pressure there was one experiment with a brine flowrate of 3 l/sec, and another with a rate of 30 l/sec; this produced total residence times of 7 minutes and 0.7 minutes. Total SiO_2 and monomeric SiO_2 were measured in water samples collected at the inlet and outlet. Salinity and pH were not reported, but saturation ratios and T-SiO_2 values suggest that there was essentially no ionized silica.

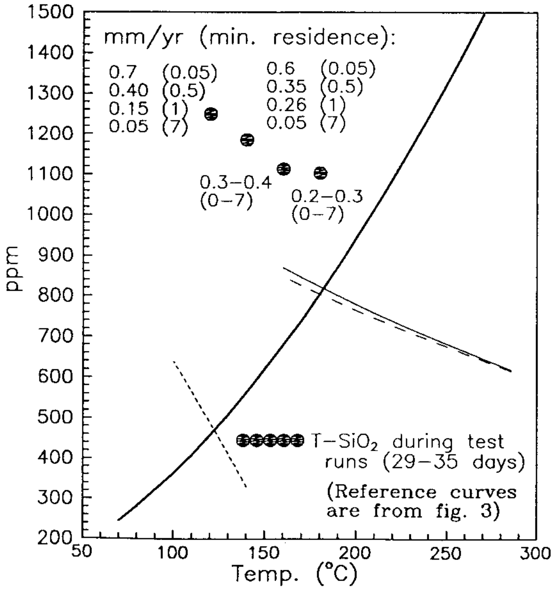

Figure 9. Silica versus temperature, scaling experiments of Mroczek and McDowell (1990).

Results are summarized on figure 9. At 180°C and 160°C, the induction time for polymerization was not reached, even at 7 minutes. Scaling rates were 0.2 to 0.3 mm/yr at 180°C (assuming density 2.2), increasing to 0.3 to 0.4 mm/yr at 160°C. At 140°C and 120°C, there was measurable polymer formation, even at the pipe inlet, and the polymer concentration increased through the pipeline; the increase at 120°C was twice that at 140°C. Therefore, scaling in the pipeline decreased dramatically along the length of the pipe, as monomeric SiO_2 was removed from solution into the suspended polymer. In all cases, the scale which formed was hard and glassy, with density about 2 gm/cc.

Mroczek and McDowell (1990) also performed some tests of silica deposition using gravel beds substituted for the open pipeline. Results were imprecise because the mass of silica deposited proved hard to measure. However, at 180°C and 160°C, there was a hard silica scale which deposited uniformly along the length of the beds. At 140°C and 120°C, there were soft, loosely adhering deposits at the bed inlet, with hard deposits downstream at 140°C, but no deposits elsewhere at 120°C. The bed inlet was a point of high flow rate and turbulence.

Summary: The scaling reports above are dominated by particle deposition. Observed rates are compiled on figure 10, showing only the rates from unaltered brine at the approximate concentration of unionized, monomeric SiO_2 in solution. The particle deposition rates are highly variable, but the pilot plant experience at Cerro Prieto may be the result of excessive turbulence. Therefore, it appears that oversaturation below about 150 ppm is unlikely to produce scale at a rate exceeding 2 or 3 mm/yr, as long as excessive turbulence is avoided. Against this the molecular deposition data of Mroczek and McDowell (1990) provide a lower limit.

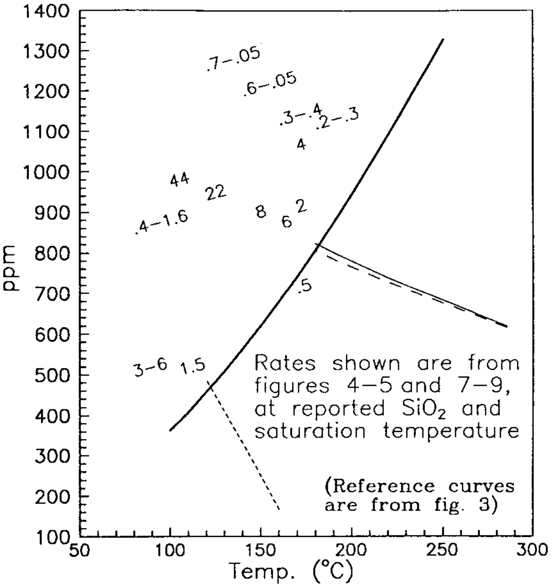

Figure 10. Silica versus temperature, showing summary of reported scaling rates.

KINETIC STUDIES

Weres and others (1982) studied polymerization and particle growth in aqueous solutions up to 100°C and containing up to 1 M NaCl (35,000 ppm Cl), to obtain rate equations for homogeneous nucleation and molecular deposition. This work produced graphs and equations for calculating molecular deposition rate and suspended particle growth rate. Jamieson (1984) has published some general mathematical relationships which describe the rate of mass transfer of particles from suspension in flowing solutions to surrounding solid surfaces. However, these have not yet been integrated with expressions for particle nucleation and growth, and calculations of particle scaling rates are not yet routinely possible.

Figure 11 (after Weres and others, 1982) shows rates of molecular deposition versus temperature and the concentration of unionized SiO_2 at a pH of 7 and NaCl salinity equivalent to about 2,400 ppm Cl. Corrections for different pH or salinity can be calculated. The quadrilateral outline on figure 11 corresponds to experimental data; rate lines outside this area were calculated. The dotted line connects points of maximum rate at given SiO_2.

Weres and others (1982) have cautioned that figure 11 and their rate equations should not be overused for scaling predictions. Their experimental data were collected at relatively low temperature, by adding known amounts of colloidal silica of known surface area to oversaturated solutions, and monitoring the loss of monomeric SiO_2. This process presented to their silica solutions a widely dispersed area of curved surfaces; thus, their experimental conditions were different from scale deposition on the wall of a pipe.

The work of Mroczek and McDowell (1990) suggests, however, that under the right conditions a prediction can be quite accurate. The predicted points for Mroczek and McDowell on figure 11 are plotted simply at total SiO_2 and temperature; measured points are plotted at temperature and observed rate. There is excellent agreement at 120°C, good agreement at 140°C, and progressively poorer agreement at 160°C and 180°C, with the predicted rates exceeding those actually observed.

Molecular deposition rates predicted for Dixie Valley and for Uenotai during 1988 (figure 11) are one to two orders of magnitude lower than the particle deposition rates actually observed and described above.

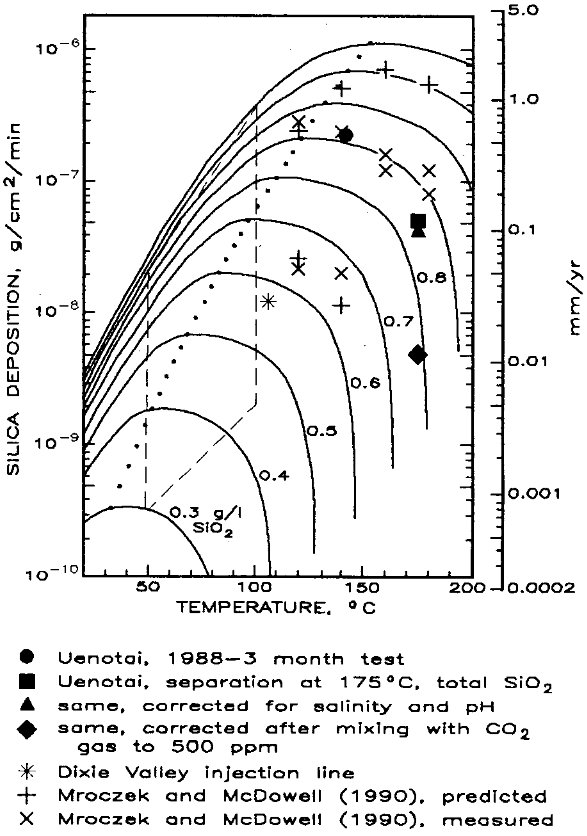

Figure 11. Rates of molecular deposition versus temperature and silica concentration (after Weres and others, 1982).

PREDICTION FOR UENOTAI

The proposed production conditions at Uenotai are illustrated by table 2 and figures 2 and 3. The figures show a particular case, while table 2 lists an average of several cases.

Table 2 : Uenotai production conditions

- 10.8 bar/182°C:
  saturation with amorphous SiO_2
- 9.3 bar/175°C:
  total SiO_2 = 850 ppm
  pH 7.2
  Cl = 225 ppm
  70 ppm oversaturation
  saturation ratio 1.1
- 8.1 bar/170°C:
  110 ppm oversaturation
  saturation ratio 1.2.
- pipeline residence maximum 20 to 45 minutes

These conditions indicate molecular deposition at about 0.1 to 0.15 mm/yr (figure 11), although this figure is approximate. Furthermore, it is expected that molecular deposition will be more significant as a scaling mechanism that particle deposition, because pH and salinity will not be particularly high, residence time will be relatively short, and supersaturation ratio low. The indicated oversaturation is below the range applicable to the homogeneous nucleation rate equations of Weres and others (1982), which prompts their guideline that molecular deposition should be dominant. Furthermore, a comparison with nucleation rate curves for higher oversaturation (Weres and others (1982)) furthermore indicates that the induction period will not be reached.

The experimental evidence of Mroczek and McDowell (1990) suggests that scaling rates will be nearly uniform along the length of the injection pipelines, with some extra build-up possible at points of turbulence. The scale is more likely to be hard than soft. Soft scale which does develop is likely to be fairly rough, forming radial ridges transverse to pipeline flow, which cause impedance. A conservative interpretation of the general experience with injection lines elsewhere indicates that some scale should be considered probable, but not likely at rates exceeding 1 mm/yr to 2 mm/yr. Therefore, a strategy to suppress or manage the expected scale has been recommended.

SUPPRESSION BY GAS OR CONDENSATE MIXING

Gas mixing to lower solution pH and suppress scale development has been discussed above. Figure 12 is a model of dissolving various amounts of CO_2 into the injection line brine, after separating the brine from steam at 175°C. The particular case modeled starts at 50 ppm oversaturation. Between 25 ppm and 500 ppm total C in solution as CO_2, there is a dramatic drop of pH from 7.2 to 5.8, while unionized SiO_2 climbs from 822 ppm to 850 ppm and oversaturation increases from 50 ppm to 75 ppm. The increase of oversaturation is completely counterbalanced by the lowered pH, and molecular deposition rate drops from 0.15 to 0.01 mm/yr (figure 11). This should also effectively eliminate any tendency for particle formation and deposition. pH and scaling potential can be lowered further with additional CO_2, but this hardly seems necessary.

It should be noted that P_{CO2} for 500 ppm is only 1.5 bar. The 500 ppm level is achieved by mixing about 0.025 t/hr non-condensible gases (13 m^3 at 1 atm.) per 50 t/hr of water flow. At Uenotai there are a number of excess enthalpy wells, and it was calculated that the gas needed for mixing into the total injection brine flow would be supplied by only 8% of the total steam flow.

For comparison with the gas mixing, we note the following: 1) mixing 50 t/hr water flow with 17.5 t/hr condensate at 60°C also lowers the molecular deposition rate to 0.01 mm/yr, and; 2) all oversaturation in 175°C water would be removed by mixing with an equal amount of 60°C condensate, and; 3) mixing with a combination of gas and condensate may have a beneficial effect by reducing winter-time freezing of vapor in the gas line.

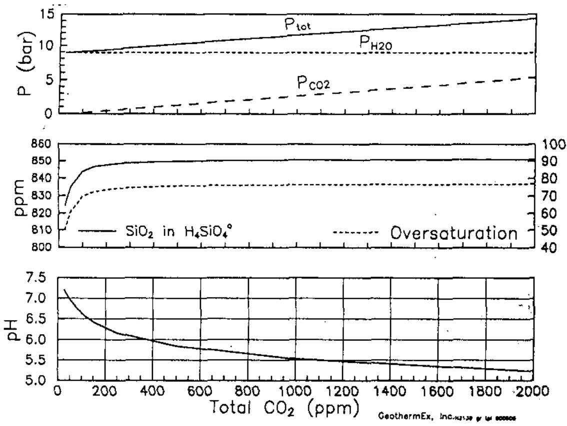

Figure 12. Effect of mixing CO_2 into the water fraction at 175°C, Uenotai well T-51.

MANAGEMENT STRATEGIES

In addition to scale suppression strategies, the following is recommended for scale management at low levels of oversaturation:

1) Design the injection system to minimize residence time and avoid turbulence.

2) Install pressure ports on injection lines to allow monitoring for scale-related impedance.

3) Install inspection ports and scaling coupon ports on the injection lines.

4) Install ports at both ends of injection lines to allow inserting a clean-out pig.

RECOMMENDATIONS FOR DATA GATHERING

It was clear from the literature review that further improvements of predictive technique will benefit from more uniformity in designing experiments, reporting results, and reporting descriptions of scale. We strongly recommend that the following be included in all reports of silica scale in production systems, pilot plants, or experimental systems:

1) Complete chemical analysis of the major elements and pH in the scale-forming water, collected at an upstream sample point.

2) Temperature, total SiO_2, monomeric SiO_2 (by colorimetry), and pH (with sample temperature) at upstream and downstream sample points. The technique of sampling and colorimetric measurement must be researched and applied carefully to give reliable results.

3) Complete analyses of the major elements and gas species in a separated water and steam sample suite, including pH, total flow enthalpy and separation P/T. The purpose of this is to allow modeling the fluid at different pressures and temperatures.

4) A short but considered description of scale morphology *vis-a-vis* the probable dominance of molecular deposition or particle deposition.

5) A description of scale thickness and location *vis-a-vis* uniformity and *vis-a-vis* flow turbulence.

6) A description of scaling rate, or total period of fluid flow in relation to scale mass or thickness. Rates should be reported both in mg/area/time and mm/yr with scale density.

7) A description of system volume and flow rate, or fluid residence time.

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APPENDIX A: FLUID MODELING CALCULATIONS - THE SILICA PROBLEM

Fluid modeling calculations for this report were done using a modified version of a thermodynamic speciation-solubility computer code described by Arnorsson and Sigurdsson (1982). Equilibrium constant data for silica species were taken from: Fournier and Potter, 1982 (quartz); Fournier and Rowe, 1977 (amorphous silica); Fournier, 1985 and personal comm. for correction to expression "r" (log K_{H4SiO4}), and; Arnorsson and Sigurdsson, 1982 (log $K_{H3SiO4-}$, log $K_{NaH3SiO4}$).

Thermodynamic codes of this type all depend on a measurement of pH at some known temperature, along with the sample composition, as a basis for calculating pH at some new temperature, with or without addition back to the sample of volatilized gases, H_2O, precipitated/dissolved minerals, etc.. In essence, the codes relate measured pH to some pH-dependent parameter which can be calculated, such as a sum of weak acid ions or "total ionizable H". Then they calculate what the new value of this parameter should be at the new temperature, and iterate to find the pH which produces that value (see review in Henley and others, 1984, chapter 7).

The correctness of pH calculations can be affected by a problem inherent in standard methods of sample analysis and input of data to the computer codes. It is not clear from a survey of the literature how widely this problem has been considered, but it has been very relevant to calculations using fluids from Uenotai.

The problem is a mismatch between measured total SiO_2 and the measured pH. The reported total SiO_2 has been measured by some technique (AA, colorimetry on a diluted sample) designed to determine all of the SiO_2 present in the water at the time of sample collection. pH is measured in a cooled sample, often several days after the sample was collected. The measured value is the result of a balance of numerous simultaneous chemical equilibria which naturally occur to keep the sample in a natural state of charge balance. In a geothermal water sample, this process is dominated by carbonate species, silica species, sulfide species, boron species, ammonia species, and others, with the silica species being particularly significant at pH above about 8. The computer code simulates this process, using the total SiO_2 measurement to calculate the contribution of the silica species equilibria. Unfortunately, if the sample is oversaturated with respect to amorphous silica, the real concentration of SiO_2 which contributes to determining pH is less than the measured total, because some fraction of the total is trapped in suspended colloidal polymers. In the real solution, the effect of this is buffered to some degree by the fact that the acidity of the polymers is higher than the acidity of monomeric SiO_2 (Marsh and others, 1975). As far as we know, this is not quantified in any of the existing computer codes.

The result is that the codes may overestimate the contribution of silica species to the parameter which they use later to determine pH at some different temperature. The size and impact of the miscalculation increases with increasing oversaturation, and increasing ratio (silica species/carbonate species). The existence of the miscalculation becomes most apparent when the water is very dilute but has very high silica, as seen by comparing measured ion balance with speciated ion balance. For example, in the sample of table 1, the ion balance of species determined by analysis is +1.29%, but the speciated ion balance is greater than -12.5% (if all of the measured alkalinity is due to silica, and more negative if some alkalinity is due to carbonic acid species), because of the large amount of $H_3SiO_4^-$ calculated to be present.

For the sample of table 1, the overestimation results in calculating a reservoir pH (at 285°C) which is too high by as much as 0.4. This is seen by first calculating reservoir speciation using the measured pH and SiO_2. The result is pH 7.40/285°C. Next, take the same sample, charge balance the analytical species with Cl^-, then adjust pH to get a speciated balance. The result (pH 8.11/22°C) is ideally the pH the sample would have had were all SiO_2 present in monomeric form. Using it as input, reservoir speciation gives pH 7.0/285°C.

This adjustment procedure is risky because of sensitivity to analytical errors, but for the Uenotai samples it appeared likely to give more valid estimates of pH in the reservoir and at various steam separation conditions, than using the measured pH value.