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SIMULATION OF THE SILICA SCALING PROCESS

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ABSTRACT

Silica scale formation nearly always involves homogeneous nucleation of particles in the brine followed by transfer of the particles to the surface. Monomeric silicic acid may also deposit at a rate determined by surface reaction kinetics.

The mass transfer rates of silica particles in boundary-layer flows and the monomer deposition rates have been estimated using a simple theoretical model. This has been used to rationalise the observed scaling rates in various field tests. It is concluded that in most cases very fine particles (<10nm radius) are involved in deposition. Ohaaki brine is an exception as larger particles may form (~200nm radius).

As these field results can be explained in terms of polymerisation and particle deposition, other factors such as aeration do not appear to be involved.

The model used does not include prediction of nucleation rates, or ripening and early growth of the colloidal silica particles. This would be required for prediction of scaling rates, but further experimental data on nucleation rates would be needed to calibrate such a model.

It is noted that additional field data on silica scaling would be useful, but it is essential that the size and number of particles involved be determined and correlated with the scaling rates.

An experimental model was used to investigate particle transfer, but this work was not successful as the very fine particles involved could not be adequately simulated.

Nomenclature

Symbols:

c	silicic acid concentration in brine	mol/kg
c_e	amorphous silica solubility	mol/kg
D	Brownian diffusivity of particle	m^2/s
H	diameter or hydraulic diameter of duct	m
k	mass transfer coefficient	m/s
k_1, k_2, k_3, k_4	coefficient due to particular transfer mechanism	m/s
m_{OH^-}	hydroxide ion concentration	mol/kg
N	number-density of particles in brine	m^{-3}
r	particle radius	m
R_m	monomer (silicic acid) deposition rate	kg/m^2s
R_p	particle deposition rate	kg/m^2s
R	total deposition rate	kg/m^2s
S	particle stopping distance in Stokes flow	m
u	brine velocity	m/s
y	distance from wall	m
ν	kinematic viscosity of brine	m^2/s
ρ	brine density	kg/m^3
ρ_s	density of amorphous silica	kg/m^3
τ_w	shear stress at wall	N/m^2

Superscript: $^+$ dimensionless quantity

INTRODUCTION

Silica scaling is a universal problem in the exploitation of geothermal fields producing brines and brine/vapour mixtures, and has largely inhibited the use of waste heat from discharge waters in these fields. It is a major design factor in all plant using these fluids; more so now than formerly as reinjection of spent brine is becoming universal. For example, the separation temperature at Ohaaki has been set at 150°C to avoid any silica problem in pipelines and reinjection wells. It is apparent that considerably more energy could be extracted from this brine.

On initial flashing, the brine may be supersaturated with silica in the form of monosilicic acid, $Si(OH)_4$, which can deposit onto surfaces as amorphous silica (AS). The rate of this deposition process is controlled by the kinetics of the dehydration/deposition reaction occurring at the surface:

$$Si(OH)_4 \rightleftharpoons SiO_2 + 2H_2O \qquad (1)$$

The excess silicic acid can also come out of solution in the form of spherical AS particles which form by homogeneous nucleation. The silica/water system is unusual in that this spontaneous nucleation in the bulk solution is generally more rapid than either direct deposition onto surfaces or heterogeneous nucleation onto dust motes, metal ions, etc. The AS particles undergo a process of Ostwald ripening while they are less than ~10nm in radius, after which they grow at the same rate as surface scale. This growth depends on the supply of excess $Si(OH)_4$ in solution. Nucleation rates are lower at high temperatures, so generally low-temperature polymerisation results in large numbers of small particles, while at high temperatures fewer but larger particles are formed.

The time required for particle nucleation and growth varies considerably with temperature, silica concentration, and pH. It is generally of the order of hours, but nucleation begins immediately on formation of the supersaturated brine and is often significant in the first few minutes. In some brines, notably at Ohaaki, polymerisation may be complete in about one hour.

When the brine is passed through pipelines, heat exchangers, and other equipment, particles nucleate and grow progressively. Monomer ($Si(OH)_4$) deposition continues at a reduced rate as the excess monomer is transferred to the particles. The particles themselves can reach the surface, impelled by Brownian diffusion, turbulence in the brine flow, or gravity. If these processes are rapid, the polymerization may increase the rate of scale formation to much higher values than would be expected for the monomer alone. On the other hand, if transfer of particles to the walls is ineffective, then polymerisation reduces the scaling rate due to removal of excess monomer.

In this work both physical and theoretical models of the scaling process have been used in an attempt to predict the scaling rate expected when a partially or completely polymerised brine is passed through a tube

THEORETICAL MODEL

In partly polymerised brine, monomer and particles deposit together so that:

$$R = R_m + R_p \qquad (2)$$

The first requirement for calculating scaling rates is to predict the rate of monomer deposition R_m for a given temperature and brine chemistry, i.e. the reaction rate for Equation 1. Bohlmann et al. (1980) have studied the kinetics of this reaction in synthetic brine, using columns packed with a silica substrate. The empirical equation which summarises their results is:

$$R_m = 1.20\,(c - c_e)^2\, m_{OH^-}^{0.7} \qquad (3)$$

This is based on experiments in the temperature range 60°C to 120°C, using synthetic brines with up to 1.0 mol/kg NaCl. There is therefore some uncertainty in applying it to natural brines or outside this temperature range; however, no other relevant experimental data are available. The AS solubility c_e can be calculated, with allowance for Ionisation of $Si(OH)_4$ at high pH if appropriate. To estimate the hydroxide ion concentration, the calculation methods of Glover (1982) have been used to adjust the solution equilibria to pipeline conditions. These calculations have been incorporated in a BASIC program.

The rate of particle deposition R_p is affected by several different modes of transfer from the turbulent core of the flowing fluid, through the boundary layer, to the wall. The most important factor affecting transfer is the inertia of the particle in relation to the structure of the boundary layer. The velocity profile in a turbulent boundary layer flow can be standardized by writing it in dimensionless form. The distance from the wall, y, is divided by the quantity ν/u^*, called the length scale of the boundary layer, and the velocity is divided by u^*, where u^* is the shear velocity given by $u^* = \sqrt{T_w/\rho}$. The standard velocity profile is illustrated in Figure 1, for the region close to the wall. The total boundary-layer thickness is of the order of $y^+ = 500$–1000.

Flow is laminar in the region closest to the wall, called the sublayer. Thus the velocity profile is linear and $u^+ = y^+$ close to the wall. For $y^+ > 5$ approximately the flow becomes turbulent and the profile curves over to approach a constant velocity in the bulk fluid.

When a particle is released into a stagnant fluid with some initial velocity it will come to rest after covering a distance S. This distance is a measure of the inertia of the particle. For small particles introduced into the boundary layer, a common if very rough assumption is that the initial velocity normal to the wall is $0.9u^*$, given to the particle by turbulent eddying in the fluid. S can then be nondimensionalised as $S^+ = Su^*/\nu$, to compare the stopping distance with the boundary layer length scale.

It is apparent that for $S^+ \gg 5$ the large and heavy particles are easily carried through the turbulent core of the flow. For $S^+ < 5$, they must diffuse through the sublayer and so R_p will be determined by movement through the sublayer, and this step is the main barrier to mass transfer. For intermediate values, inertial projection through the sublayer is a possible mechanism but is comparatively slow.

Conventionally, diffusion or other transfer is correlated with a mass transfer coefficient k, defined as the flux of particles transported divided by the driving force for diffusion. The driving force is simply the difference in number-density between the bulk fluid and the wall. For no reverse movement, this is equal to N. Thus the flux of particles is N.k particles/m^{2}s, and the mass transfer rate is given by:

$$R_p = \frac{4}{3}\pi r^3 \rho_s\, N.k \qquad (4)$$

k has the dimensions of velocity and so can be nondimensionalised as $k^+ = k/u^*$.

Four modes of particle transport through the boundary layer have been identified as possible contributors to silica scaling:

1. Turbulent diffusion. The mass transfer rate of particles in turbulent flow conditions can be estimated by analogy with the diffusion-controlled transfer of solutes to and from flowing fluids. An experimentally-based correlation (Treybal 1968) similar to the Dittus-Boelter equation for heat transfer is used:

$$\left(\frac{k_1 H}{D}\right) = 0.023 \left(\frac{Hu}{\nu}\right)^{0.83} \left(\frac{\nu}{D}\right)^{0.33} \qquad (5)$$

2. Convection through the sublayer. Cleaver and Yates (1975) have given theoretical predictions of the transfer rate of fine particles ($0.1 < S^+ < 10$) through the sublayer, based on the observations of Kline et al. (1967). The normally laminar flow in the sublayer is interrupted by occasional, random bursts of turbulence which are generated close to the surface. These provide a mechanism for convection both towards and away from the surface. A simple model of the flow pattern in one of these turbulent bursts gives the following equation:

$$k_2^+ = 0.2125\, \frac{\rho}{\rho_s}\, S^+ \exp\,[0.533\, S^+] \qquad (6)$$

3. Inertial projection across the sublayer. Kneen and Strauss (1969) made a correlation of experimental deposition data using aerosols, in which they assumed that a projection mechanism was operating. Their semi-empirical correlation was:

$$k_3^+ = 0.00047\, (S^+)^2 \qquad (7)$$

   This generally predicts lower scaling than for Equation 6.

4. Brownian diffusion through the sublayer. For $S^+ < 0.1$, the higher diffusivity of the small particles means that they are transported rapidly by Brownian motion. On the assumption that the sublayer extends to $y^+ = 5$, this can be calculated:

$$k_4^+ = \frac{D}{5\nu} \qquad (8)$$

These four mechanisms are combined to predict the overall mass transfer coefficient k, using the simple network model shown in Figure 2. Particles are assumed to move to $y^+ = 5$ by turbulent diffusion, and then the three modes of transport through the sublayer are regarded as alternative paths for deposition. The total mass transfer coefficient is then easily calculated:

$$k = k_1 \Big/ \left(1 + \frac{k_1}{k_2 + k_3 + k_4}\right) \qquad (9)$$

These equations have been used in the form of a simple BASIC program to calculate the scaling rate and particle growth expected when brine flows through a short length of duct. This may be a tube or a noncircular section such as an open drain, but caution is needed with noncircular ducts as Equation 5 is based on circular tube data. To use the program, an estimate of the size and number-density of particles at the inlet to the duct must be provided. The scaling rates, and the changes in number and size of particles and monomer concentration through the duct, are calculated.

APPLICATION TO FIELD DATA

For each experiment, the possible range of input values for particle radius (r) and number-density (N) were first evaluated by estimating:

i) the size of a critical nucleus formed by homogenous nucleation,

ii) the maximum size formed by growth according to Equation 3,

iii) the maximum number permitted by the supply of excess monomer.

Within these limits, varying sizes and numbers are tried for their effect on scaling.

1. Heat exchanger fouling.
Three field trials using tubular heat exchangers have been simulated. These were made at Svartsengi and Hveragerdi in Iceland (Gudmundsson and Bott 1979) and at Ohaaki (Jamieson, Drew, and Could 1982). In all three tests, the amount of growth permitted by (ii) above is very small, so that any particles involved must have been deposited while close to their initial nucleus size. The sizes and numbers for which the program predicts the observed scaling rates are given in Table 1.

2. Wairakei scaling test.
Mahon, Klyen, and McDowell (1975) report a field test made at Wairakei, in which brine was passed through a holding tank and then through a 150-mm pipe. This test is of interest because high scaling rates were found in the pipe although Equation 3 indicates much lower scaling. The critical radius in this brine is $\sim$1nm, and the maximum growth for the holdup time used gives a radius of 13nm. Between these limits, the equations 5 to 9 above were used to calculate the expected scaling for various particle sizes and number-densities.

The results of this simulation are shown in Figure 3. The deposition rate predicted by Equation 3 for non-polymerised brine ($\sim 4.5 \times 10^{-8}$ g/cm^{2}min) is shown as a horizontal line "NO POLYMERISATION" and the range of experimental results is also indicated. Results of the simulation are shown as curves of constant number-density N. For each assumed value of N, there is a maximum radius at which all the excess monomer originally present has been assumed to be polymerised. This limit is indicated by a broken line.

The approximate range for which the observed scaling rates can be rationalised is thus indicated by the small cross-hatched area, i.e.

$$1 < r < 3 \quad \text{(nm)}$$
$$10^{15} < N < 10^{16} \quad (\text{cm}^{-3})$$

3. Ohaaki (BR22) scaling tests.
Brown and McDowell (1982 and 1983) made a series of experiments aimed at evaluating the effects of aeration and pH adjustment on scaling. Secondary separated brine from BR22 was passed through 25-mm pipes after holdup for various periods. This simulation has been applied only to their 1982 conditions (~ 115°C) with no aeration or pH adjustment. In the Ohaaki brine, rapid kinetics for Equation 3 mean that the expected monomer scaling rate is high at $\sim 7.5 \times 10^{-7}$ g/cm^2 min. The scaling rates found in the experiments were significantly lower than this. The rapid deposition also means rapid particle growth, so with holdup the potential exists for growth of particles with radii of $\sim$ 200nm.

When the simulation is made and plotted in the same manner as before (Figure 4) it is seen that the predicted mass transfer coefficients are low and the net result of polymerisation is to reduce the scaling. The experimental rates can be rationalised approximately with particle radii of 100-150nm, and number-densities of the order of 10^{10} cm^{-3}.

EXPERIMENTAL MODEL

Equation 5 is considered the least reliable part of the mass transfer calculation, especially where non-circular ducts are concerned. A correlation analogous to Equations 6 to 8, relating the turbulent diffusion of a particle towards the sublayer to its inertia, would be a more satisfactory approach. An experimental rig was built in which air flowed over a flat surface, and polystyrene foam beads were released into the airstream (Figure 5).

The range of conditions of interest for this work was $10 < S^+ < 100$ for which the turbulent part of the boundary layer is a major resistance to mass transfer, i.e. k_1 is expected to determine the transfer rate. As a result of using air instead of water, the density of the beads was ~ 30 times the fluid density, as compared to ~ 2 times the fluid density for AS in water. Measurements of the velocity profiles achieved with the rig indicated that the range that would be attained was $\sim 150 < S^+ < 1000$, for 1mm beads.

Some deposition experiments were made with this arrangement, on the basis that a correlation obtained in this range could be extrapolated to lower S^+ values provided the main mechanism of scaling was the same throughout the range. However, the theoretical modelling (above) done concurrently with this, indicated that in most cases the particles involved in scaling are very fine ($r < 10$nm) which means that S^+ is less than 0.1. In this range, Brownian diffusion is crucial to the scaling rate. Extrapolating results from $S^+ \sim 150$ to this range is out of the question.

DISCUSSION

The results of simulating the heat exchanger tests can be related to the holdup used in each experiment. At Ohaaki, the brine was undersaturated on reaching the heat exchanger, and nucleation could only have started after significant cooling in the tube. At Svartsengi, the heat exchangers were located close to the separator, and the brine entered seconds after flashing to a supersaturated condition. At Hveragerdi, the town supply of separated water was used, and had a slight supersaturation after flashing at the wellhead, 20—30 minutes before use. As indicated by Table 1, the predictions correspond to the experimental scaling rates if one assumes that monomer only was deposited at Ohaaki, and an increasing degree of nucleation occurred for the other two.

Although the nucleation and growth rates are slow for the Icelandic tests, due to low initial silica concentrations, in both cases the nucleated particles form most of the scale. The contribution of monomer deposition is $\sim$10% of the total scaling at Svartsengi, and <2% at Hveragerdi. It is notable that hard vitreous scales were formed although most of the depositing silica was in particulate form. The Hveragerdi deposits had transverse ripples, which were responsible for high pressure drop. From this simulation, it appears likely that this is the result of particles being the only scaling mode, with monomer deposition almost completely suppressed. Similar ridging occurs in reinjection pipeline deposits at Ohaaki (Taylor 1981) where polymerisation is almost complete in the pipe.

The two field tests described have shown that this approach is capable of rationalising the scaling rates observed in the field, for various scaling conditions. This gives rise to conclusions about the state of polymerisation which produced the observed scaling; however, these are not tested as the brine was not analysed for particle size and numbers at the time.

Where particle growth is limited either by slow kinetics or by lack of time, the very small particles ($r < 10$nm, $S^+ < 1$) are deposited rapidly because of their high diffusivity. This can account for scaling rates much higher than predicted by kinetics. The Icelandic tests and the Wairakei experiments are examples of this, and the experience of scaling in the majority of fields appears to be of this type. In the minority of field experiments where larger particles (radius up to 500nm) were formed, low mass transfer meant that scaling rates were lower than predicted by Equation 3. In the data reviewed for this project, only Ohaaki experiments were of this type.

Since this model is able to rationalise the field data, there appears to be no need to introduce those factors which have not been simulated. Several other factors have been postulated as affecting silica scaling:

1. Aeration. It was suggested many years ago that the high scaling rates in open drains at Wairakei right be associated with exposure to air, since similar brines in closed pipes gave little trouble. Several attempts to induce faster scaling by aerating brines (e.g. Brown and McDowell, 1982) have failed, however, and it is possible that the Wairakei scaling could be explained by polymerisation and hydrodynamic effects.

2. Electrostatics. AS scales and particles are expected to carry a negative surface charge at the pH valves common in geothermal brines. For the charge densities determined experimentally at room temperatures (Iler, 1979) mutual repulsion would be expected to prevent any particle deposition. The surface charges existing in saline brines at high temperatures are not known.

3. Particle adhesion. Ponding has sometimes been used to reduce deposition. It has been assumed (e.g. Mahon et al., 1975, Rothbaum et al., 1979) that highly polymerised brines tend to deposit less because of weak adhesion when large particles reach the surface and little or no monomer is available to cement them to the existing scale. This work has shown that such low scaling rates can be explained in terms of slow transfer to the surface.

A predictive model would need to cover the entire process of nucleation, ripening, growth, and simultaneously scaling. Instead, in this work, only the scaling itself has been described. There are two possible lines for further work using this general approach:

1. Additional field test work could be undertaken to determine scaling rates in particular fields. If the results of this testing are to be useful for predictive purposes, it is essential that the progress of polymerisation through the plant, and particularly the size range and number-density of the depositing particles, should be determined and correlated with the scaling rates.

2. The model could be extended to include the earlier stages of polymerisation. This would allow prediction of scaling without making assumptions about the state of polymerisation at the inlet to the section of plant which is being simulated. However, it is unlikely that such a model could be developed and made reliable without experimental work to address the problems of predicting nucleation rates, and providing more accurate kinetic information.

CONCLUSIONS AND RECOMMENDATIONS

The simple scaling model described can successfully rationalise observed scaling rates both for cases where these are higher and lower than the expected chemical deposition rates. Factors, such as aeration and electrostatic effects, which have not been included, are not significant.

High scaling rates appear to be associated with very fine AS particles. These reach the surface by Brownian diffusion. Larger particles (diameter up to ~500nm) are associated with lower scaling.

The experimental simulation was not useful as it was not possible to simulate fine particle scaling.

The type of scale formed cannot be predicted. However, as a general observation it is suggested that any significant monomer deposition results in hard vitreous scales. Rippled, spiky, or massive deposits only form when particle scaling dominates and almost no monomer is deposited.

This type of model may be useful for scaling rate prediction. However, it would also be necessary to simulate the nucleation and ripening of AS particles, and this will probably require experimental data on nucleation rates in geothermal conditions.

Additional data on the kinetics of Equation 1 in geothermal conditions would also be useful. Equation 3 is entirely empirical, and based on a narrow range of conditions.

Additional field date on silica scaling should be obtained. However, it is essential that such experiments investigate polymerisation and the brine characteristics at the point of scaling. The size and number of polymers in the brine must be known if scaling rate data are to be usefully interpreted.

TABLE 1: HEAT EXCHANGER FIELD TRIALS

	Holdup (minutes)	r_{min} (nm)	r_{max} (nm)	N (cm^{-3})	R_{m_2} (g/cm^2min)	R_{p_2} (g/cm^2min)
Ohaaki	0	0.5	0.7	$< 0.1 \times 10^{14}$	0.7×10^{-7}	0
Svartsengi	< 1	1.2	1.3	0.9×10^{14}	0.26×10^{-7}	2.5×10^{-7}
Hveragerdi	20–30	0.5	0.7	19×10^{14}	0.03×10^{-7}	6.6×10^{-7}

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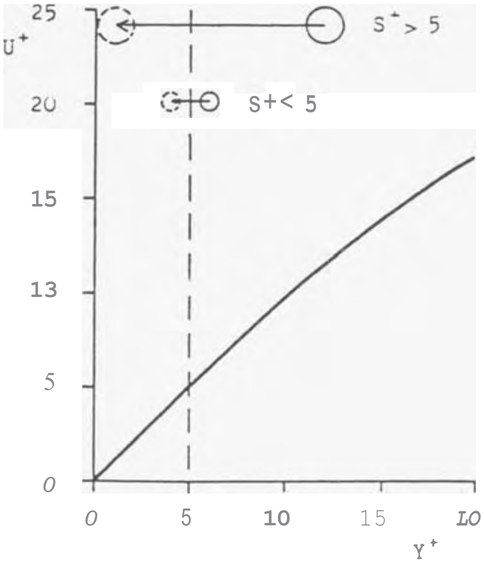

FIGURE 1 Generalised Velocity Profile

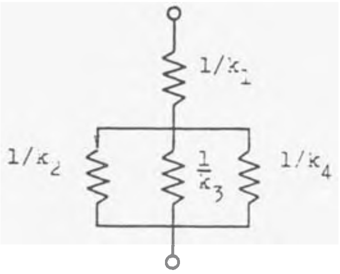

FIGURE 2 Resistance Network

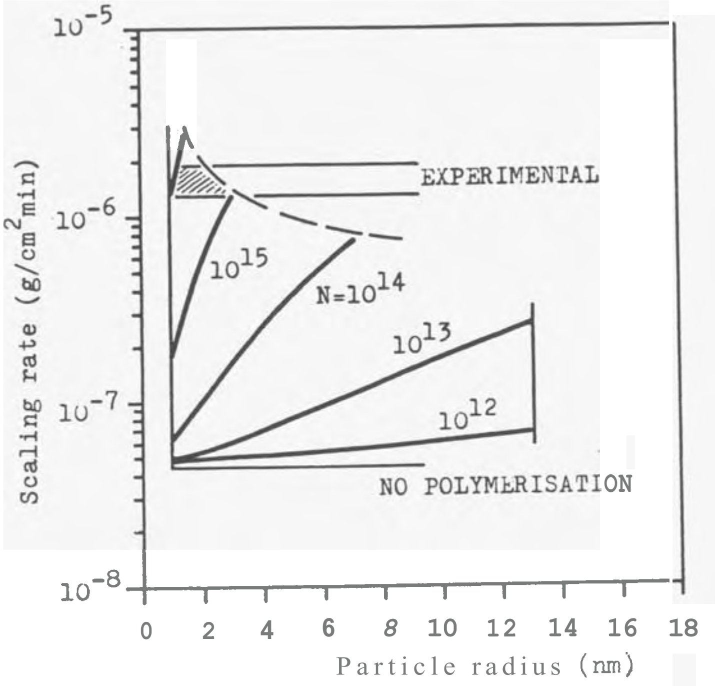

FIGURE 3 Wairakei Scaling Test 1975

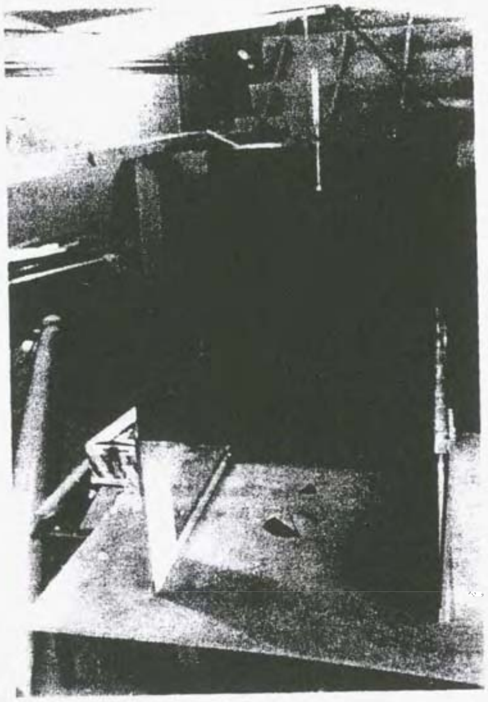

FIGURE 5 **Experimental** Rip;