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Hydro- and Electrochemical Aspects of Silica Colloid Deposition from a Turbulent Flow onto a Rough Wall

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Abstract

Silica scaling is a highly undesirable process accompanying the extraction of geothermal energy. The mechanisms of transport and attachment of silica nanoparticles governing this process remain poorly understood. The comparative analysis of the existing experimental and theoretical data suggested the theory underestimates the convective transport of the particles on to a rough wall. The proposed hypothesis of specific inertial deposition of the nanoparticles onto roughness elements (not accounted in the current theory) was tested. The analytical solution of the corresponding mass transfer problem showed that this additional transport is significant enough to explain observed anomalies of the silica scaling process and, therefore, must be accounted in future numerical simulations.

Introduction

Silica scaling is a process of deposition of natural colloidal silica from a cooled geothermal fluid [1]. It leads to deterioration of the heat exchange and pressure drop in the geothermal plant equipment. Silica scaling poses a multimillion problem for geothermal power generation industry.

The rate of silica scaling depends on hydrodynamic and chemical conditions. Such parameters as temperature, pH and concentration of the dissolved minerals in the geothermal fluid control both the rate of the silica precipitation from the fluid and the stability of the formed nanoparticles [4]. The probability of a particle forming a bond with a surface upon collision is inversely proportional to its stability.

Meanwhile, the rate of the particle – wall collisions in general is determined by their transport within the flow. The transport, depending on the particle inertia, geometry and flow rate can be dominated either by diffusion or inertia of the particles [3]. Specific relationships between the transport rate and particle size, surface and flow properties distinguish these two mechanisms. Current theory of particle transport suggests that the diffusion transport should dominate for the conditions relevant to geothermal silica scaling [1, 5]. If so, decrease of the transport rate as particle size increases is predicted.

The scaling rate may be expressed as a product of the rate of transport of silica particles to the surface and the probability of their permanent attachment to it [5]:

$$[Scaling\ rate] = k \times [Transport\ rate] \qquad (1)$$

here k is the attachment probability. The following subsections show how particles stability and transport rate are expected to vary with their size. The combined effect is speculated to be a lower theoretical scaling rate for bigger particles.

This speculation is then tested here by direct comparison with the experimental data. The measurements of the rate of colloidal silica deposition in two flow scenarios – a cylinder in a cross-flow [1] and pipe flow [5] - indicated consistent increase of the scaling rate with particle size and flow rate. Furthermore, the morphology of the silica scale observed in these experiments suggests significance of the inertial effects in colloidal silica deposition.

These discrepancies between the theory and experiment suggested underestimation of the transport rate in current theory. Therefore, the possibility of the direct inertial deposition of silica nanoparicles onto an individual scale protrusion is examined by means of non-dimensional analysis. As a result, the rate of the additional inertial deposition onto a rough surface (not accounted for in current particle transport theory) is quantified as a function of particle size, surface roughness and fluid friction velocity.

Attachment Probability

Depending on the solution pH, silica colloids can carry uncompensated surface charge due to the ionization of the surface silanol groups. The presence of the charge of the same sign on all particles, and on wall surfaces covered with amorphous silica, results in an electrostatic potential barrier which the particles need to overcome to form the bond. As a result, not all collisions lead to aggregation or particle attachment to a surface [4].

The stability was determined theoretically within the Smoluchowski-Fuchs framework by considering a problem of the particles diffusion in the presence of the electrostatic interparticle potential described by the DLVO theory [4]. The colloid stability $W = 1/k$ was shown to decrease with increasing ionic strength of the solution (salt concentration) and with decreasing particle size d.

It was found that in silica sols with the ionic strength IS=30mM and pH=7.5 typical for geothermal brine only about 1 in 10^8 collisions result in deposition of 125 nm particles on a smooth surface. For a particle half this diameter, W is 4 orders of magnitude smaller.

The standard DLVO theory predicts instability of small particles at a higher concentration of dissolved salts. Thus, at IS=67mM, representative for the pipe scaling experiments presented in the next section, particles smaller than 60 nm in diameter are expected to aggregate/deposit upon each collision. Although, our direct measurements [4] showed that the actual aggregative stability in this case is significantly higher: W=6×10^8 for 20 nm and W=4×10^9 for 10 nm particles. This was explained by presence of an additional steric repulsion between the particles.

Another important factor affecting the probability of particle deposition is the heterogeneity of a surface. The stability of the "particle - rough wall" collisions was suggested to be an average between the corresponding values for the "particle-particle" and "particle-smooth wall". Therefore, for the hydrodynamic and chemical conditions of the experiment [1] attachment probability for 125 nm particles is taken to be $k=10^{-5}$.

The attachment probability of 40 nm particles used in the pipe scaling experiments [5] was measured [4]: $k=10^{-8}$.

General Theory of Particle Transport

Uncharged particles suspended in a turbulent flow are transported to a stationary wall by two main mechanisms: diffusion and convection (the latter is sometimes called inertial transport). The flux of particles in the direction y normal to the wall for fully developed flow can be expressed as [3]:

$$j = -(D_B + D_T)\frac{d\bar{c}_p}{dy} + \bar{c}_p \bar{V}_{py}^c \qquad (2)$$

The first term on the right-hand side of equation (2) is the diffusion due to a gradient in the particle concentration and the second term represents convective transport arising from particle inertia. The particle convective velocity $\bar{V}_{py}^c$ in the y direction normal to a wall is determined from the particle momentum equation which accounts for the gradients in turbulent intensity, shear induced lift and other external forces. The particles are assumed not to interact with each other, or with the wall.

The numerical solution of equation (2) and corresponding particle momentum equation for the deposition on a smooth parallel surface allowed Guha [3] to find a relationship between the non-dimensional deposition velocity V_{dep}^+ and particle relaxation time τ_p^+ (figure 1). The non-dimensional deposition velocity V_{dep}^+ is the wall particle flux j normalized by bulk concentration of particles c_p^0 and fluid friction velocity υ_0:

$$V_{dep}^+ = j / c_p^0 \upsilon_0, \qquad (4)$$

with $\upsilon_0 = \sqrt{\varepsilon/\rho_l}$ determined from flow conditions (here ε denotes wall shear stress).

The dimensionless particle relaxation time is a measure of the particle's ability to deviate from fluid motion:

$$\tau_p^+ = \frac{\rho_p d_p^2}{18\rho_l}\left(\frac{\upsilon_0}{\nu}\right)^2 \qquad (5)$$

where $\rho_p = 1500\, kg/m^3$ and ρ_l are the particle and water densities correspondingly and ν is the water kinematic viscosity.

Smaller particles follow the fluid motion more closely than bigger particles, thus as they get closer to the wall they lose the y component of their convective velocity much faster than bigger particles. For very small particles this eventually leads to existence of a thin region close to the wall in which particle transport continues only by Brownian diffusion. This region is called the diffusion sublayer.

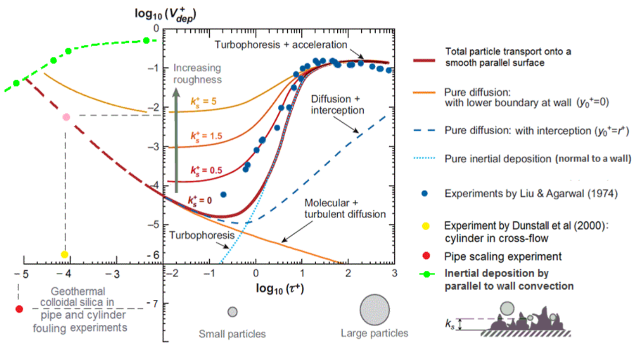

Figure 1. Classification of the particle transport mechanisms [3] and the rate of an additional convection

Guha has also shown that particle deposition velocity is significantly affected by the roughness of the surface to which particles are transported (figure 1).

Real walls, having roughness elements protruding from their surface, experience higher mass transfer than ideal, perfectly smooth walls. The particles need to be transported through the diffusion sublayer over shorter distance to reach the roughness elements with effective height k_s. This increases transport of smaller particles for which this diffusion sublayer exists (see figure 1 for $log_{10}\, \tau_p^+ \leq 0$).

New steel surfaces with $k_s = 0.05\, mm$ have dimensionless effective roughness height $k_s^+ = k_s \upsilon_0 / \nu$ equal 16 and 10 in cylinder [1] and pipe scaling experiments [5] correspondingly. Whereas if the effective height of roughness elements is equal to the average height of silica scale ridges $k_s \approx 0.12\, mm$ these values increase to $k_s^+ = 45\, and\, 25$.

According with Guha's calculations [3] the dimensionless deposition velocity increases from 10^{-3} for a smooth wall to at least 10^{-2} for a rough one at $\tau_p^+ = 10^{-4}$ and from 10^{-2} to 10^{-1} correspondingly at $\tau_p^+ = 10^{-5}$ (figure 1).

Experimental Studies of the Silica Scaling

Silica deposition onto carbon steel cylinders in a cross-flow of natural geothermal brine was studied by Dunstall et al. [1]. The deposition rate was found to increase with the particle size and flow rate (figure 2). Silica deposition was revealed to form ridges of scale parallel to the cylinder axis and perpendicular to the flow direction. The height of the silica ridges was found to vary significantly around the cylinder circumference (figure 3 a). The maximum height of ~0.25 mm was reached at approximately 21° from the upstream stagnation point.

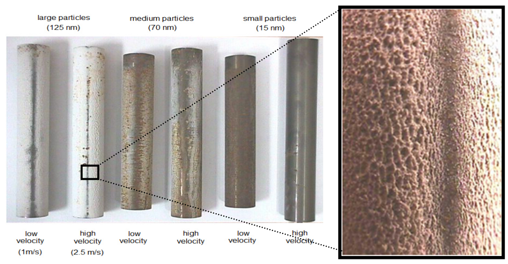

Figure 2. Geothermal silica scale on cylinders in cross flow [1]

The rate of deposition of 125 nm particles from the flow with bulk velocity of 2.5 m/s can be calculated from the scale height measurements reported in [1] (figure 3). Assuming that the curve in figure 3a represents the height of a continuous film of silica deposit, we find the total deposition rate to be 2.2×10^{-9} kg/s per 1m of cylinder length. In reality, though the curve follows the edges of the highest silica ridges and there are voids in-between these ridges (figure 2 b).

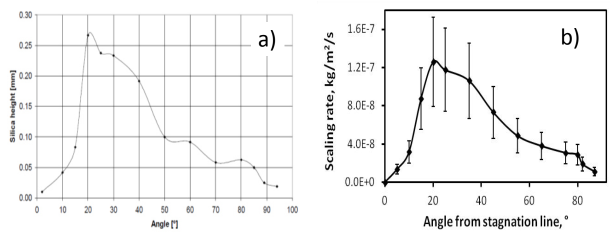

Figure 3. a) Distribution of silica scale [1] and b) corresponding scaling rate on a cylinder in cross flow

Therefore, to find real deposition rate the unknown void fraction of the silica deposit was estimated to be 0.25 with an uncertainty of ± 50 %. The total deposition rate was then evaluated to be $(1.6\pm0.6)\times10^{-9}$ kg/s per 1 m length of the 25mm cylinder or $(4.2\pm1.6)\times10^{-8}$ kg/s/m^2. The dimensionless deposition velocity found by dividing this averaged value by bulk concentration of the silica particles ($c_p^0 = 0.25$ kg/m^3) and by average shear velocity on the cylinder surface ($\upsilon_0 = 0.14$ m/s) equals 1.2×10^{-6}.

The experimental studies of the silica scaling in mild steel pipes [5] revealed similar particle size/flow rate effects. Higher deposition rate was associated with bigger particles and higher flow rate. Particularly for 40 nm particles the scaling rate was directly measured (by weighing the deposits) to be 1.7 $\cdot 10^{-8}$ kg/s/m^2. When normalized with the corresponding shear velocity ($\upsilon_0 = 0.17$ m/s) and concentration of the silica particles ($c_p^0 =$ 1.6 kg/m^3) this gave dimensionless deposition rate of 6.3 $\cdot 10^{-8}$.

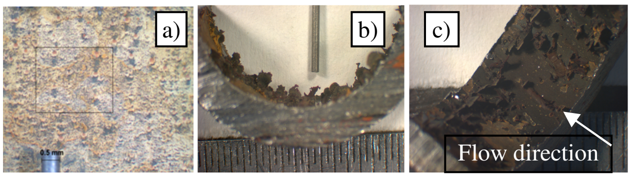

Figure 4. Silica scale on internal surface of a carbon steel pipe: a) small particles/low flow rate and b, c) big particles/high flow rate

Similar to the cylinder in cross-flow experiments the deposition of silica was highly non-uniform in pipe experiments. This was expressed in growth of numerous relatively large (0.1-1mm) protrusions and few yellowish deposits in the areas in-between them (figure 4). At high flow rate the deposition of bigger silica naniparticles formed spanwise consecutive ridges inclined towards oncoming flow. This configuration of the tower type protrusions suggests that they were formed by inertial deposition. This mechanism of deposition contributes to the growth of the leading edge of a protrusion. The diffusion, in turn, dominates the particle transport behind them, in the wake zone where the mixing, and thus, mass transport are significantly accelerated.

Interestingly, the dimensionless scaling velocity measured in two reported experiments [1,5] is about 4 and 7 orders of magnitude smaller than V_{dep}^+ predicted by particle transport theory for the corresponding values of τ_p^+ (figure 2). This difference can partially be explained by moderate stability of the investigated colloidal silica discussed in Introduction. Although, when calculating theoretical scaling rate using equation 1 with measured stability values it was noticed that the theoretical transport rate is underestimated. It must be slightly higher in order to provide the observed deposition rate for the given particle stability.

Moreover, for the relevant particle size range the theory of particle transport predicts significant decrease of the deposition rate with increasing particle size. The experimental scaling rates, in turn, had opposite trends. This can be explained first, by the increase of attachment probability with particle size. However, the standard DLVO theory predicts the opposite – higher stability for bigger particles, and the theory of electrosteric stability is not developed well enough to make a reliable conclusion regarding stability dependence from the particle size.

A second possible explanation is that current theory of particle transport does not include all relevant mechanisms. We hypothesize that the inertia of particles in the diffusion dominated size range, although has insignificant effect on convection normal to a wall, still can promote their tangential (parallel to the wall) convection onto roughness elements protruding from the wall. To best of our knowledge this particle transport mechanism was not accounted for by Guha in figure 2.

This hypothesis may also explain the spatial distributions of the scale on the cylinder observed in the experiment (figure 3). Higher scaling rate observed at the locations with higher wall shear stress. First, the thickness of the diffusion boundary layer is smaller here which makes the effect of existing surface roughness higher. Second, at the locations with higher wall shear stress particles have higher tangential velocity and thus more significant additional convection. The next section is dedicated to the assessment of the feasibility of this hypothesis.

Analysis of Particle Deposition on a Single Scale Protrusion

The tangential component of convective particle transport during silica scaling is evaluated analytically by considering a problem of particle movement with a flow around a single hemispherical protrusion on a wall. First, to simplify the analysis we neglect the effect of particle redistribution by Brownian motion on the particle transport by the fluid motion. This allows treatment of the total particle transport as a simple superposition of the diffusion and inertial transport.

Second, the role of the turbulent pulsations in particle motion is also neglected. The convection of particles in direction normal to a wall due to the turbophoresis, as well as other inertial mechanisms, is already accounted for in Guha's result (figure 1). Meanwhile, the effect of the turbulence pulsations on the tangential convective transport of particles can be safely neglected if the protrusion is smaller than the thickness of the viscous boundary layer δ_v. Otherwise, intense pulsations of the instantaneous tangential velocity in near wall region ought to affect the inertial transport of particles onto the protrusion. This complex effect is a subject for a future study. Only the mean flow parameters are considered here.

The particles are assumed to deviate from fluid streamlines only due to their inertia. The ability of particle to deviate is measured by its relaxation time - the time constant in the exponential decay of the particle velocity due to drag - $\tau_p = \frac{\rho_p d_p^2}{18\mu_l}$ – here ρ_p is the particle density, d_p is the particle diameter and μ_l is the dynamic viscosity of water .

Meanwhile, the probability of a particle to collide with an obstacle is determined by the dimensionless Stokes number: $\mathrm{St} = \frac{\tau U_0(y)}{d_c}$ - here d_c is the characteristic dimension of the obstacle and $U_0(y)$ is x component of the fluid velocity away from the obstacle as a function of wall distance (y).

The typical height of scale protrusions observed on figure 5 a is accepted as the characteristic length $h = d_c = 0.25\, mm$. The near wall velocity distribution of pipe flow with average velocity of 2.8 m/s is calculated as:

$$U_0(y) = \begin{cases} \frac{y\upsilon_0}{\nu} & y < \delta_v \\ 2.44\upsilon_0 \ln\left(\frac{y}{\xi}\right) + 8.5 & y > \delta_v \end{cases} \tag{6}$$

where the friction velocity υ_0 is calculated using Serghide's solution for the friction factor for a full-flowing circular pipe [7]. The surface around a protrusion is assumed to have effective sand roughness of size $\xi = 0.05$ mm – typical for a clean carbon steel surface. Although, silica scale on the surface around the protrusions (figure 4a) contributes to its higher roughness. This results in steeper flow velocity rise outside the viscous sublayer and thus higher local St number.

Figure 5 presents values of the Stokes number calculated for the abovementioned flow conditions and variable particle and obstacle sizes.

These values can be used to find the ratio of particles travelling towards the frontal area of the obstacle that will collide with it. This ratio is called the collection efficiency ϵ. Its dependence on the St number for spherical collectors is available from previous experimental and numerical studies [6,2]. Figure 5 b shows that the ratio of particles that collide with the roughness to the total number of particles travelling towards its frontal area increases with the St.

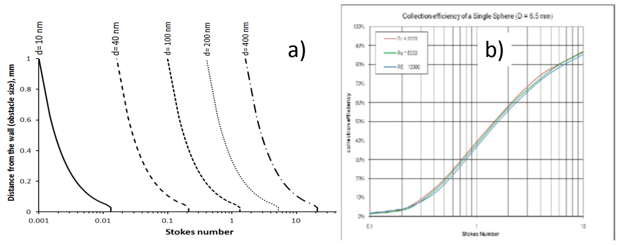

Figure 5. a) St number for the different size particles as a function of scale element size; b) collection efficiency as function of St number [6]

For the sake of simplicity the relationship between the collection efficiency and St number obtained in [6] for various size spherical collectors in uniform flow is transferred onto our case of a hemisphere in a boundary layer. The main difference is that in our case collection efficiency is a function of wall normal distance.

Taking this into account and recalling the definition of the collection efficiency the rate of particles inertial transport on a single hemispherical protrusion can be shown to be

$$j^{in} = 2c_p \int_0^h \epsilon\left(St(y, d_p)\right) \cdot U_0(y) \cdot \sqrt{h^2 - (y + dy)^2}\, dy \quad (7)$$

This integral can be calculated for the known near wall velocity distribution $U_0(y)$ (equation (6)), bulk concentration of the particles ($c_p = 1.6\ kg/m^3$), collection efficiency $\epsilon(y, d_p)$ [6] and variable particle size (50÷100 nm). This will yield the rate of inertial deposition onto a single hemispherical protrusion. Corresponding particle transport rate per unit area, additional to that represented in figure 1, is a product of this integral value and number of the protrusions per unit area. According to figure 4a this number can be estimated as 0.2×10^6 protrusions per m^2.

Finally, Figure 2 compares rates of the additional inertial particle transport and other transport mechanisms. It is evident that additional convection can explain the difference between experiment and theory for the big, but not small particles in the tested size range (see Table 1). This could be an outcome of many assumptions made above regarding particle transport onto the scale protrusions or inaccuracy in the adopted particle stability values.

Particle size	Experimental scaling rate, $kg/m^2/s$	k × [Transport rate in [3]], $kg/m^2/s$	k × [Transport rate in [3] + additional convection], $kg/m^2/s$
125 nm	$1.2\cdot10^{-6}$	$5\cdot10^{-7}$	$3.4\cdot10^{-6}$
40 nm	$6.3\cdot10^{-8}$	$3\cdot10^{-9}$	$3.2\cdot10^{-9}$

Table 1. The experimental and theoretical scaling rates

Conclusions

This work reports the analysis of the mass transfer mechanism specific to deposition of silica nanoparticles on a rough steel surface. Particle transport is a determining step in silica scale formation which causes fouling of geothermal power plant equipment. Improved understanding of this phenomenon ought to result in a reduction of associated operational costs for geothermal power stations.

Previous experimental studies of the silica scaling were compared here with the predictions of the current particle transport theory. The experimental scaling rate was identified to be 4-7 orders of magnitude lower than the theoretical transport rate. This difference was explained by the high stability of the silica nanoparticles as reported elsewhere – only 1 in 10^5-10^9 particles colliding with the surface actually attach to it.

In fact, the theoretical particle transport rate was found to be insufficient to explain the observed rate of deposition for such stable particles. Moreover, the particle size relationships observed in the experiments and predicted by the theory were contradictory. The theory suggested domination of the diffusion transport, and thus lower transport rate for bigger particles, in the relevant particle size range. The experiments, in turn, indicated faster scaling for larger particles.

These persistent discrepancies between the experiment and theory together with some specifics of the silica scale morphology stipulated the necessity of additional investigation. Therefore, a hypothesis of the presence of significant, additional inertial mechanism of the particle transport is tested in this paper.

Guha in his calculations [3] has considered only the wall-normal component of the convective particle transport. We have evaluated its tangential component. This was done by first, finding particle flux onto an upstream side of a single scale protrusion. Second, it was multiplied by the experimentally derived surface density of the protrusions to give the estimated transport rate for this mechanism.

In spite of the simplified approach, this additional convective particle transport was found to be of the same order of magnitude as the total transport rate obtained by Guha. The rate of this additional convection was also shown to increase with particle size. Its magnitude is significant enough to explain the discrepancy between the experimental scaling rate and product of the theoretical transport rate and particle attachment probability. Therefore, this specific inertial mechanism of particle transport should be included into future numerical silica scaling simulation.

Acknowledgments

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References

[1] Dunstall, M., Zipfel, H. & Brown, K. L., The onset of silica scaling around circular cylinders, *World Geothermal Congress*, Kyushu-Tohoku, Japan, 2000, 3045-3050.

[2] Frank, H., Günter, D. & Fritz, E., Inertial impaction of aerosol particles on single and multiple spherical targets, *Chem. Eng. Technol.*, **17**, 1994, 88-94.

[3] Guha, A., Transport and Deposition of Particles in Turbulent and Laminar Flow, *Annu. Rev. Fluid Mech.*, 2008, 311–41.

[4] Kokhanenko, P., Jermy, M. & Brown, K., Silica aquasols of incipient instability: synthesis, growth and long term stability, *Journal of Colloid and Interface Science,* in review.

[5] Kokhanenko, P., Masuri, S., Jermy, M., Sellier, M. & Brown, K., Hydrodynamics and electrochemistry of silica scaling, *34th New Zealand Geothermal Workshop*, Auckland, New Zealand, 2012.

[6] Martin, S., Particles Deposition on an Array of Spheres using a Hybrid Euler/Lagrange CFD Method, *Trainee Report,* Paul Sherrer Institute, 2009.

[7] Serghides, T.K, Estimate friction factor accurately, *Chemical Engineering Journal*, **91(5)**, 1984, 63–64.