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Thermodynamics and kinetics of silica scaling

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ABSTRACT

Silica scaling is probably the principal factor limiting the extraction of energy from high temperature geothermal systems. Silica exists in a number of polymorphs from quartz through to opal A (or amorphous silica). The thermodynamics of the solubility of quartz and amorphous silica with variations in temperature, salt content, pH and pressure are discussed. However, in silica saturated geothermal brines, silica normally precipitates from oversaturated brines as a colloid. The colloid formation and properties are discussed together with mechanisms for colloid deposition. .

1. INTRODUCTION

All deep geothermal fluids contain dissolved solids. The amount varies considerably, from about 100 g/tonne (Iceland) to about 250 000 g/tonne (Salton Sea). These chemicals are dissolved in the water under conditions of elevated temperature and pressure. During exploitation of the field, the fluid is brought to the surface and heat is extracted in one of two ways. Either the heat is transferred to a second working fluid (a binary system) or steam is extracted. In the first case, the geothermal fluid is conductively cooled and as the solubility of most compounds is lower at lower temperatures, there is the possibility of depositing some of the dissolved species. In the second case, as well as cooling the geothermal fluid, we have concentrated it by removing up to say 30% of the water as steam, and therefore the likelihood of scaling is much greater at the same temperature.

This scaling has a number of detrimental effects. Pipes become blocked and have to be replaced, wells become blocked and need to be drilled out, environmental problems arise, reinjection wells become "tight", and the use of waste heat is prevented.

Except for a few isolated cases, there are only two main chemical compounds that are responsible for massive scaling in geothermal operations. These are silica (SiO_2) and calcium carbonate ($CaCO_3$).

Silica deposition can be conveniently split into two sections. The **thermodynamics** and **kinetics** of silica deposition. The thermodynamics of silica solutions allows the prediction of what must eventually happen when equilibrium is reached. The kinetics try to explain how fast equilibrium is achieved. We will consider each of these aspects in turn.

2. THERMODYNAMIC CONSIDERATIONS

Silica exists in a number of different forms; Quartz, tridymite, cristobalite, amorphous silica and others. Quartz is the predominant form of silica present in nature. The surrounding rocks of most geothermal reservoirs contain quartz, and this will dissolve in the hot water. Above about 230°C for some time, it is generally considered that quartz is in equilibrium between the solid and dissolved species, i.e. the reaction:

$$\mathbf{\underset{Quartz}{SiO_2(s)} + 2H_2O \leftrightarrow \underset{silicic\ acid}{H_4SiO_4(aq)}}$$

is in equilibrium. The reaction is temperature dependent and follows the equation:

$$\log C = -1309/T + 5.19$$

Where C = silica concentration in mg/kg and T = absolute temperature (K). This approximate equation is valid for 0 - 250ºC. The solubility of quartz at saturated water vapour pressure reaches a maximum at about 340ºC in pure water. An equation valid for the quartz solubility from 20ºC to 330ºC is given by Fournier (1986):

$$t = -42.196 + 0.28831{*}C - 3.6685\times10^{-4}{*}C^2 + 3.1665\times10^{-7}{*}C3 + 77.034{*}\log C.$$

Where t = ºC and C = silica concentration in mg/kg.

2.1 Amorphous silica

When the hot water is underground, it is in equilibrium with quartz. However, the form of silica normally precipitated at the surface is **amorphous silica**. Amorphous silica has no crystalline structure and is **more soluble** than quartz. The solubility of amorphous silica has been measured at the saturated vapour pressure of water (Fournier and Rowe, 1977). This solubility is given by:

$$\log C = -731/T + 4.52 \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where C and T are the same as for the quartz solubility. The solubility of quartz and amorphous silica as a function of temperature is shown in Figure 1. Therefore when geothermal waters are brought to the surface, the difference in solubility between amorphous silica and quartz allows a considerable drop in temperature before the solution becomes saturated with respect to amorphous silica.

The solubility equations for quartz and amorphous silica have been calculated at the saturated vapour pressure of pure water. As the concentration of other dissolved species is increased (e.g. in NaCl solutions) the solubility of both quartz and amorphous silica is decreased.

Quartz and amorphous silica are end members. There are other forms of silica, but they are generally poorly crystalline. In order of increasing solubility, they are quartz, chalcedony, α-cristobalite, Opal CT, Opal A (amorphous silica).

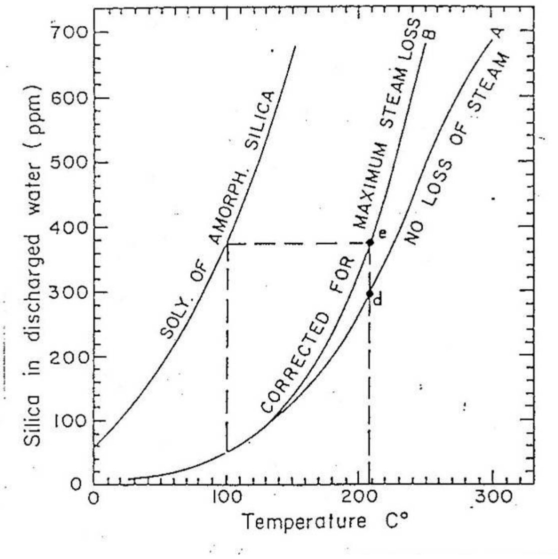


Figure 1: From Truesdell and Fournier (1976)

Quartz has a crystal structure where every silicon atom is surrounded by four oxygen atoms. Each oxygen atom is then connected to another separate tetrahedral silicon atom and the pattern is repeated in three dimensions. When this dissolves in water, discrete molecules of H_4SiO_4 are formed. These have a structure where each Si atom is bonded tetrahedrally to four hydroxyl groups. The hydrogen atoms can dissociate, so silicic acid is a weak acid according to:

$H_4SiO_4 \Leftrightarrow H^+ + H_3SiO_4^-$

Log K for this reaction is given by:

$\log K_1 = -2549/T - 15.36 \times 10^{-6} T^2$ (T = abs K)

The charged $H_3SiO_4^-$ ion is very soluble in water, so there is a large increase in silica solubility at higher pH as the silicic acid becomes dissociated (Figure 2).

As the pH is increased, further dissociation is possible to form $H_2SiO_4^{=}$, however, these are only significant at very high pH ($\log k_2 = -11.0$ at 100ºC).

If the effects of the second order ionisation are neglected, and it is assumed that the solubility of silica is due entirely to the reaction:

$$SiO_2 + 2H_2O \Leftrightarrow H_4SiO_4$$

Then the solubility of amorphous silica as a function of pH can be derived as:

$$S = C\,[1 + \{10^{pH} * K_1 / \gamma_{(H3SiO4-)}\}]$$

Where C = solubility in mg/kg from eq 1

K_1 = dissociation constant above

$\gamma_{(H3SiO4-)}$ = activity coefficient of $H_3SiO_4^-$

The activity coefficient is calculated from the extended Debye Huckel equation and the ionic strength of the solution. A typical example of the solubility calculation is shown in Figure 2 (Henley, 1983)

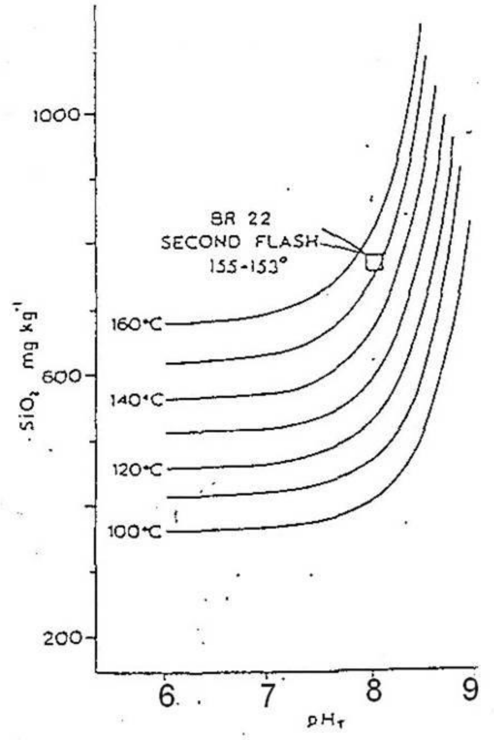


Figure 2: Calculated amorphous silica solubility for Br22 well (I = 0.047)

As can be seen, the solubility of amorphous silica increases markedly as the pH_T is increased. If a two stage extraction of steam (double flash) rather than a single flash is utilised, more CO_2 is extracted into the vapour phase, and consequently, the pH of the remaining solution is raised. This then increases the solubility of amorphous silica.

The difference in solubility between quartz and amorphous silica allows exploitation of geothermal systems without the possibility of silica scaling. Remember that the deep fluid is saturated with respect to quartz, but under-saturated with respect to amorphous silica. As this fluid undergoes adiabatic steam loss rising in the well and in flash plant, there are two separate effects.

1. The concentration of silica in the separated water is increased by the effect of steam loss.

2. There is a drop in temperature of the separated water as the pressure is lowered and thus the solubility of silica is lowered.

The **silica saturation temperature** is the temperature at which the separated water reaches saturation with respect to amorphous silica. This is an important temperature because if the geothermal fluid is separated above this temperature, then silica scaling cannot occur.

One further required definition is the **silica saturation index (SSI)**. This is defined as the ratio of the silica concentration in the brine divided by the equilibrium amorphous silica solubility at the conditions prevailing. If SSI >1.0 then silica scaling is possible, if SSI <1.0, then generally, silica scaling will not occur.

3. KINETIC ASPECTS OF SILICA DEPOSITION

3.1 Introduction

In the previous section, we have been looking at the equilibrium chemistry of silica solutions. In practise, silica solutions sometimes take very long times to reach equilibrium. For instance, although all separated waters are supersaturated with respect to quartz, it is almost never seen as a deposit in geothermal power production despite the fact that it is the stable form. The kinetics of silica deposition is concerned with the **rate** at which a supersaturated solution will deposit silica. This area of silica chemistry is much less predictable than the thermodynamics, and is not well understood or quantified. However, the thermodynamics represent the worst possible case and the kinetic effects tend to allow more flexible solutions to the problems of silica scaling.

Laboratory experiments and field observations have shown that there are a number of factors that affect the kinetics of silica deposition. Some of the more important are:

1. Degree of supersaturation
2. pH
3. Temperature
4. Flow rates
5. Aeration
6. Other ions in solution

In general, the deposition of amorphous silica follows one of two possible mechanisms:

1. The preliminary formation of a colloid and its subsequent precipitation.

2. Direct deposition on to solid surfaces.

The product of the first mechanism is a porous, low bulk density, sometimes not very adhesive, softer deposit, while the second tends to give a vitreous, very hard, difficult to remove, high density product.

3.2 Colloids

Colloids are defined as small particles of a substance suspended in an immiscible medium. The suspended particles are small enough that they remain suspended and can be stable for large periods of time. The type of colloid that silica forms is a solid (the silica particle) suspended in a liquid (the brine). Typical solid colloid particles range in size from 3 – 3000nm. The particles are kept from settling with gravity by Brownian motion. Other types of colloid are liquid in liquid (emulsions), gas in liquid (foam), liquid in gas (aerosol).

The science of colloids is primarily involved with the science of the surface between the colloid and the suspending medium. It is a very old science, and yet has developed markedly only recently with the surge in “nanotechnology”. The word colloid comes from the Greek word for glue - κολλα - from the use of gums which are colloidal suspensions. Solid colloids suspended in water can be defined as either hydrophilic (water-loving) or hydrophobic (water-hating). Proteins, other macromolecules and silica are mostly hydrophilic. An example of a hydrophobic colloid is ink.

If the colloidal particles are well dispersed and remain in suspension for long periods of time, they are called “colloidally stable”. Such a system can, however, be influenced by electrolyte or other surface acting compounds that can lead to co-agulation and sedimentation. (flocculation and coagulation). Hydrophilic colloids can be thermodynamically stable, but hydrophobic colloids cannot.

Silica colloids can form **sols**, which are discrete silica particles, **aggregates**, which are collections of particles or **gels**, which are silica particles connected over long ranges (Figure 3).

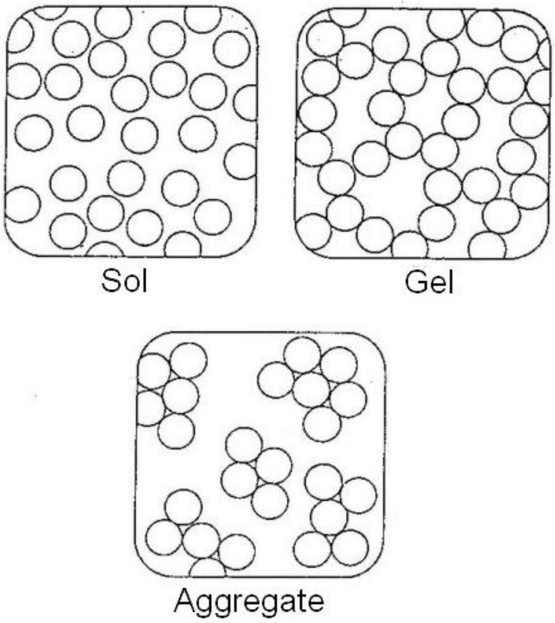


Figure 3: Forms of silica colloids.

3.3 Silica colloid formation

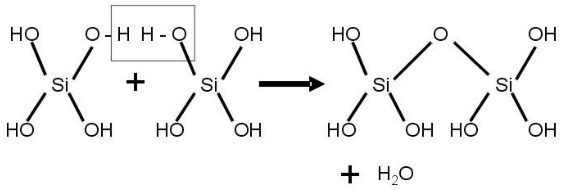
As it is currently understood, the formation of the stable colloidal suspension takes place in three phases:- *NUCLEATION, RIPENING and GROWTH.*

NUCLEATION:

When two silicic acid molecules come together in a supersaturated solution they can combine to form a dimer $H_6Si_2O_7$ and a water molecule:

$$H_4SiO_4 + H_4SiO_4 \Rightarrow H_6Si_2O_7 + H_2O$$

What happens is:



This reaction is catalysed by hydroxyl ions (OH^-) and so can be retarded by the addition of acid to lower the concentration of OH^-.

This reaction is the first stage in the **polymerisation** of silica. Polymerisation continues to form trimers, tetramers, etc. The bonds that form the polymerisation are randomly chosen and consequently the large polymer that is formed has no crystal structure. Because only two **silica** molecules (two monomers) are necessary to start the reaction, this mechanism is called **homogeneous nucleation**. Often, if the supersaturation is low, there is a time lag before nucleation proceeds. This is sometimes referred to as an "induction period".

The chemical driving force for the nucleation reaction is the oversaturation of silicic acid in solution. The greater the degree of oversaturation (ie the larger the SSI) the faster nucleation proceeds.

RIPENING:

As polymerisation proceeds, the size of the now spherical particles increases by bonding of more monomeric silica particles from the supersaturated solution. After a while, the number of monomeric molecules left in the solution is reduced to the point where further nucleation is prevented. At this stage, the process of "Ostwald ripening" takes place: the smaller particles redissolve and the larger particles continue growing. The larger particles keep growing at the expense of the smaller particles until a critical size is reached where further growth is not controlled by the size of the particle. This ripening process thus controls the **number** of particles that eventually form. It also tends to produce particles of a uniform size (a “monodisperse” colloid).

GROWTH:

As further monomer becomes available (eg by further cooling) then the particles already formed can grow. Usually, no further particles are formed - ie nucleation will not recommence - once a ripening phase has been completed unless there is a large oversaturation again. The energy required to form a new particle is greater than the energy required to latch on to an already formed particle. The final size of the colloidal particles can range from ~0.003 to 3 µm.

Typical silica colloids are shown in Figure 4. Note that all the colloids are the same size.

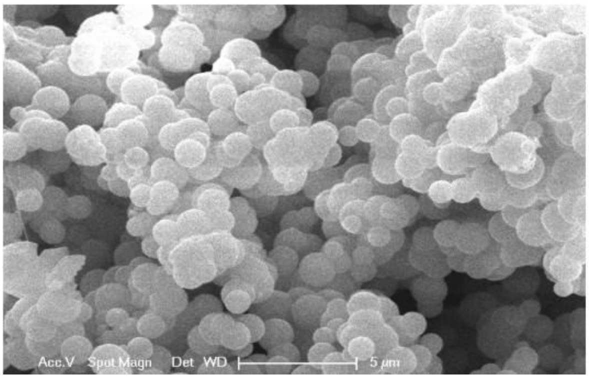


Figure 4: Typical silica colloids

3.4 Silica colloid properties

Individual silica colloids are spherical as shown in Figure 4. This minimises the surface energy. The colloids in normal solutions are very stable as they have a negative surface charge. This charge can prevent agglomeration by electrostatic repulsion, and is responsible for the stability of silica colloids.

The colloid particle size depends on the degree of oversaturation and the rate at which the oversaturation is reached. If there is a sudden large increase in SSI, than a large number of nuclei are formed, and this leads to a large number of small particles. On the other hand, if the SSI is increased relatively slowly, then fewer nucleii are formed, and then excess silicic acid molecules grow the already formed particles which leads to a smaller number of larger particles.

3.4 Silica colloid deposition (scale formation)

The colloid formation and growth is the initial stage of silica scale deposition. Although the theory of silica colloid formation is relatively well understood, the mechanism of silica deposition is far less well characterised. The mechanism by which a silica colloid is transported through the brine to a solid surface (pipe wall, formation rock) and is then bonded to that surface is not well understood. However, some factors are known. It should be borne in mind that once a monolayer of silica molecules has been deposited on the surface, then silica scaling is an interaction between like silica particles.

3.4.1Colloid/colloid interaction:

The interaction between charged silica colloid particles can be calculated with DLVO theory. This theory can quantify the energy of interaction as two charged particles approach each other. A typical interaction is shown in Figure 5.

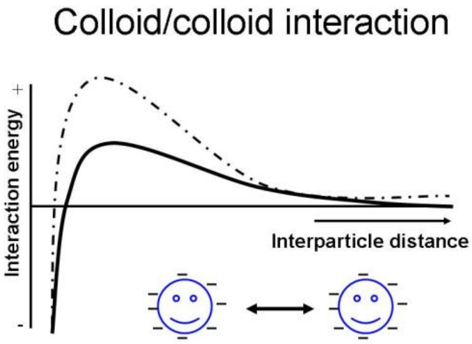


Figure 5: Colloid interaction with separation

As two colloids approach each other, the energy of interaction increases as the electrostatic forces increase. However, when the particles get close to each other (Angstroms), the force turns from a repulsive electrostatic force to attractive "London" and "Van der Waals" forces which will bind the particles together. The ease with which particles agglomerate or deposit depends on the magnitude of the repulsive force barrier shown in Figure 5. It is possible to alter the surface properties of the colloid by adding chemicals and these can increase the energy barrier to overcome – as shown by the dotted line in the figure. This is the basis of dosing with chemical dispersants.

3.4.2 Effects of other ions

Two effects are important with respect to other ions in solution.

Firstly, in brines with a high ionic strength, such as the Salton Sea brines, positive ions such as Na^+, are attracted to and surround the colloid and can reduce the electrostatic interaction to a point where there is no repulsion and agglomeration is very rapid. That is, there is no energy barrier to overcome and the colloid interaction is like that shown in Figure 6. Rapid agglomeration leads to either rapid scaling, or in solution leads to gravity settling of the agglomerated colloids as their size and molecular weight cannot be supported by Brownian motion.

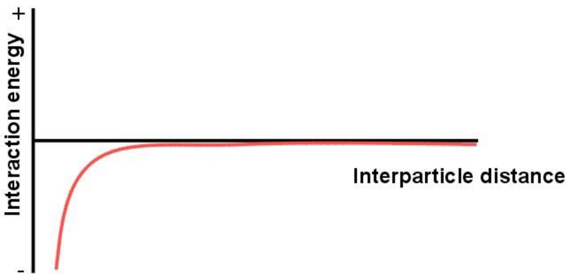


Figure 6: Colloid interaction in high ionic strength

The second effect is due to small amounts of highly charged ions. The negative surface charge attracts cations in solution and these can act as a bridge between neighbouring colloid particles essentially bonding them together to form a scale or a larger agglomerate that is gravity deposited. Trivalent ions such as Al^{3+} and Fe^{3+} are especially effective in this regard. In experiments with As_2S_3 colloids, the following table shows minimum coagulation concentrations (mmoles/L) for a number of ions:

$AlCl_3$	0.062
$FeCl_3$	0.136
$CaCl_2$	0.649
$MgCl_2$	0.717
KCl	49.5
NaCl	51.0

It can be seen that the +3 ions are extremely effective at colloid agglomeration. In geothermal environments, the small amount of aluminium is almost quantitatively deposited with silica. As well as having a very high charge, the Al^{3+} ion has an ionic radius almost identical to Si^{4+} and is incorporated readily into the colloid. The aluminium can reduce the solubility of amorphous silica (Gallup, 1977)

3.4.3 Effect of colloid particle size and fluid velocity

Experiments at Wairakei have shown that colloid particle size can have an enormous effect on silica scaling. As shown above, it is possible to control the particle size of the silica colloids by controlling the rate of nucleation. It was found (Brown and Dunstall, 2000) that very small colloids of the order of 15 nm particle size showed virtually no scaling, whereas colloids with a particle size of 120 nm showed significant silica scaling. In the same experiment, the effects of fluid velocity were investigated and showed that increasing the fluid velocity increased the silica scaling. A very visual proof is shown in Figure 7. In this experiment, three particle size colloids (120nm, 70nm and 15nm), and two fluid velocities (2.5 m/s and 1 m/s) were exposed to the same total silica concentrations at the same temperature for the same time period.

Figure 7: Silica scaling under controlled hydrodynamic and colloid particle size. From L to R: large particles - slow velocity, large particles - fast velocity, medium particles - low velocity, medium particles – fast velocity, small particles – low velocity and small particles – fast velocity.

From the figure, it is obvious that the small particles cause very little silica scaling.

3.4.4 Measurement of silica polymerization

It is possible to measure chemically the amount of **monomeric** (i.e. H_4SiO_4 molecules) silica present in solution, without interference from the **polymerised** silica present. Therefore we can measure the rate of disappearance of monomeric silica and this will equate to the rate of formation of the colloidal particles. An example of the polymerisation rate of the same brine at different temperatures is shown in Figure 8.

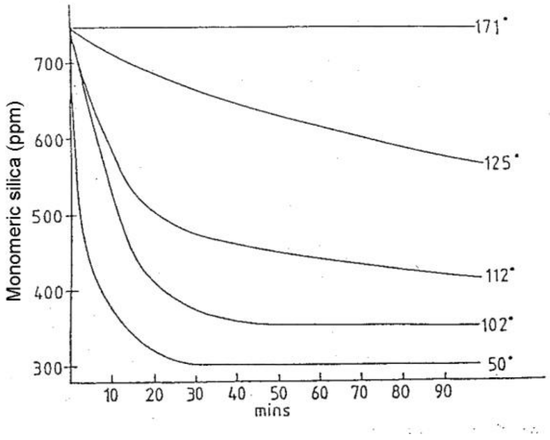


Figure 8: Rate of disappearance of monomeric silica as a function of time at different temperatures.

It can be seen that at 171ºC, the fluid is above the silica saturation temperature and no polymerisation is taking place. As the temperature of the brine is decreased, the SSI is increased and the rate of polymerisation is also increased.

The rate of silica polymerisation can also be measured as a function of pH. An example is shown in Figure 9. In this example, the silica polymerisation has been delayed at the lower pHs, while at the normal pH, silica polymerisation is very rapid.

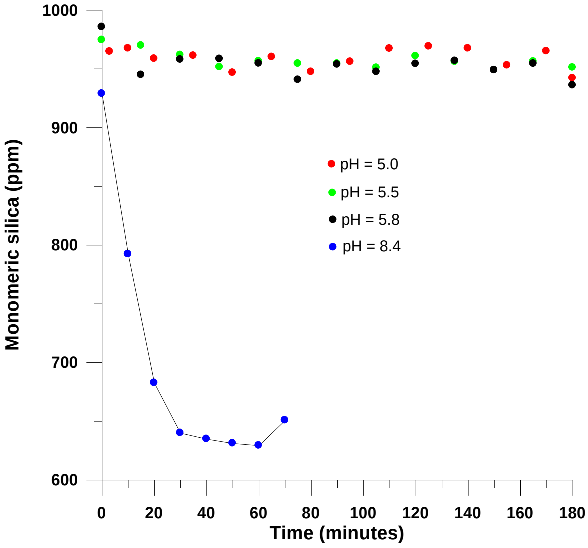


Figure 9: Silica polymerisation as a function of pH

3.5 Monomeric silica deposition

This is sometimes called “direct deposition’. This is the direct deposition of monomeric silica molecules, without the formation of a colloid. It typically forms a very hard, dense, amorphous vitreous scale that can be very difficult to remove. The deposition rate is slow compared to colloidal deposition, with typical scaling rates in the order of 0.5 mm/year. It is not normally a problem in reinjection pipelines, but can cause loss of heat transfer in heat exchangers in binary power plants.

4.0 TREATMENTS TO COPE WITH SILICA SCALING

Because of the very large volumes of water to be treated, any process to stop silica scaling must be relatively cheap. There are a number of possible methods for minimising or halting colloidal silica scaling. However, all are not necessarily practical or economic.

4.1 Avoidance of amorphous silica saturation

The difference in solubility between quartz and amorphous silica allows energy to be extracted while still keeping the amorphous silica undersaturated. Even at low levels of supersaturation (SSI < 1.2 say), the level of scaling may be acceptable, or there may be a sufficiently long induction period, that silica scaling is avoided in reinjection wells and reinjection pipelines. Until recently, this was practised at nearly all geothermal power developments. It does restrict the energy that can be extracted from a geothermal resource, and more recent geothermal developments have utilised methods to cope with brines which are oversaturated with amorphous silica.

4.2 Inhibition of colloid formation

The rate of colloid formation decreases at lower pH. When the pH is lowered to 4.5 – 5.0, the polymerisation can often be halted for several hours. However, this is only a kinetic effect, and the silica will eventually polymerise and possibly deposit. The target pH for this method is usually a compromise between retarding the silica polymerisation and having acceptable corrosion of carbon steel. Normally, sulphuric acid is used as it is available at 98% concentration and has two protons available. However, where there is a possibility of anhydrite ($CaSO_4$) deposition, hydrochloric acid can be used.

Where brines are reduced to low temperatures at a low pH, for instance in binary plant heat exchangers, there is the possibility of stibnite (Sb_2S_3) deposition.

4.3 Aging of the brine

If the dissolved silica is allowed to become fully polymerised, then the colloidal silica scaling has been found to be less. Experiments by Mroczek (1994) have shown that silica scaling is greater when the silica is polymerising than it is if the silica is fully polymerised. In practise, this technique can lead to large particle sizes for the colloid, which can lead to a greater hydrodynamic effect.

4.4 Colloid stabilisation

By adding chemicals to the solution, it is possible to change the surface characteristics of the colloid such that the energy barrier to approach another colloid is increased (see Figure 5). There is currently a number of programs in progress to develop and test these ‘colloidal dispersants’.

4.5 Removal of the silica

A number of different methods are available to treat the colloidal suspension to precipitate and remove the silica. This sometimes has the added advantage of removing other objectionable compounds, like arsenic. Addition of lime (CaO) is one possible treatment that has received some attention. However, the major use of silica removal is in the CRC process for the Salton Sea brines.

4.6 Raising the pH

Silicic acid becomes soluble by converting the dissolved silica to the silicate ion. This involves raising the pH by adding caustic. Experiments at Ohaaki (Lichti et al, 2000) showed that at 100°C, silica scaling is prevented by raising the pH at 100ºC to 9.0. There seemed to be no problems with corrosion of steel in this experiment. The major drawback is the cost of the alkali.

4.7 Rapid cooling of the brine

As mentioned above (section 3.4.3) rapid cooling of the brine can produce very small colloids which have been shown to be less likely to form a scale. The kinetics are normally such that the brine must be cooled in a matter of seconds rather than minutes for the particle size to be sufficiently small. A system of very rapid cooling has been tested by Gunnarsson and Arnorsson (2005).

5.0 MEASUREMENT OF COLLOID PROPERTIES

As characterisation of the colloid becomes important, some of the colloid properties need to be measured. Probably the two most important parameters are the zeta potential (ζ) and the colloid particle size.

Zeta potential is measured by electrophoresis – measurement of the motion of a charged particle in a static electric field. Zeta potential is defined as the potential drop across the mobile part of the colloid’s electrical double layer that is responsible for electrokinetic phenomena. It is basically a measurement of the specific charge on a colloid.

Colloid particle size is measured in situ by light scattering techniques. Silica colloids vary in size from ~ 1 nm to 5000nm. The size is measured by the technique of dynamic light scattering (DLS), sometimes called photon correlation spectroscopy (PCS). Coherent laser light is directed into the solution and the scattering of the light when detected, either by transmission or reflection, gives a measure of the particle size. It is a complex technique that requires knowledge of other factors such as viscosity, refractive index, temperature etc in order to interpret the scattering. However, a number of manufacturers have developed instrumentation that is relatively easily operated.

Some instruments can measure both zeta potential and particle size.

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