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Gunnuhver hot spring at Reykjanes geothermal field

Kevin Brown

MINERAL SCALING IN GEOTHERMAL POWER PRODUCTION

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MINERAL SCALING IN GEOTHERMAL POWER PRODUCTION

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PREFACE

The UNU Visiting Lecturer in 2013 was Dr. Kevin Brown, who is among the leading geothermal specialists of New Zealand and has been involved with geothermal energy for 32 years. Since 1997, he has been a partner in GEOKEM – a consultancy based in New Zealand which specializes in geochemistry of geothermal systems and environmental geochemistry. In this capacity, he has consulted to government research organizations, private companies, UNDP and the World Bank widely around the world, as well as in New Zealand. The principal thrust of his research and consulting work is the chemistry of geothermal systems, and particularly, the chemistry of geothermal systems developed for power production and geothermal power station geochemistry. He has specialised in mineral deposition in geothermal development, and has undertaken many research projects on the behaviour of silica in geothermal developments. Allied to this interest, is work relating to the mineral extraction from waste geothermal brines. Other research interests include 4 seasons in Antarctica studying the geochemistry of meltwater ponds and their ice cores in the Dry Valley regions – from very hot water to very cold water for a change! He has also published on the relationship between geothermal systems and epithermal ore deposits. Prior to forming the GEOKEM consultancy, he was Assoc. Professor of Geology and Geothermal Energy at the University of Auckland. In this capacity, he taught geothermal geochemistry and geochemical modelling at the Geothermal Institute. He is currently an adjunct Professor in the Geology Department at the University of Canterbury. Dr. Brown's lectures at the UNU-GTP received great interest and were very well attended by members of the geothermal community in Iceland as well as the UNU Fellows and UNU-GTP MSc Fellows.

Since the foundation of the UNU-GTP in 1979, it has been customary to invite annually one internationally renowned geothermal expert to come to Iceland as the UNU Visiting Lecturer. This has been in addition to various foreign lecturers who have given lectures at the Training Programme from year to year. It is the good fortune of the UNU Geothermal Training Programme that so many distinguished geothermal specialists have found time to visit us. Following is a list of the UNU Visiting Lecturers during 1979-2012:

1979 Donald E. White	United States	1996 John Lund	United States
1980 Christopher Armstead	United Kingdom	1997 Toshihiro Uchida	Japan
1981 Derek H. Freeston	New Zealand	1998 Agnes G. Reyes	Philippines/N.Z.
1982 Stanley H. Ward	United States	1999 Philip M. Wright	United States
1983 Patrick Browne	New Zealand	2000 Trevor M. Hunt	New Zealand
1984 Enrico Barbier	Italy	2001 Hilel Legmann	Israel
1985 Bernardo Tolentino	Philippines	2002 Karsten Pruess	United States
1986 C. Russel James	New Zealand	2003 Beata Kepinska	Poland
1987 Robert Harrison	United Kingdom	2004 Peter Seibt	Germany
1988 Robert O. Fournier	United States	2005 Martin N. Mwangi	Kenya
1989 Peter Ottlik	Hungary	2006 Hagen M. Hole	New Zealand
1990 Andre Menjoz	France	2007 José Antonio Rodríguez	El Salvador
1991 Wang Ji-yang	China	2008 Wang Kun	China
1992 Patrick Muffler	United States	2009 Wilfred A. Elders	United States
1993 Zosimo F. Sarmiento	Philippines	2010 Roland N. Horne	United States
1994 Ladislaus Rybach	Switzerland	2011 Ernst Huenges	Germany
1995 Gudmundur Bödvarsson	United States	2012 Cornel Ofwona	Kenya

With warmest greetings from Iceland

Lúdvík S. Georgsson, director, UNU-GTP

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1. INTRODUCTION

All deep geothermal fluids contain dissolved solids. The amount varies considerably, from about 100 g/tonne (for some fields in 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) in a heat exchanger, or steam is extracted to become the working fluid. 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 some of the water as steam, and once again, there is the possibility of depositing some mineral species. In both cases, as the fluid rises in the well, the physical and chemical properties can change and also lead to deposition of a scale.

This scaling has a number of detrimental effects. Pipes can become blocked and have to be reamed or replaced, wells become blocked and need to be reamed or cleaned out, environmental problems can arise, reinjection wells decrease in injectivity, and the use of waste heat can become difficult.

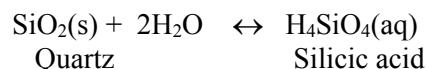
The most common mineral scales encountered in geothermal development are silica (SiO_2) and calcium carbonate (CaCO_3). In some developments, heavy metal (Cu, Pb, Zn) sulphide scaling is observed. With the increase in the use of binary plants – either as the principal source of electricity production or as bottoming plants – antimony and arsenic sulphide scaling can also occur.

2. SILICA

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 tries to explain how fast equilibrium is achieved. We will consider each of these aspects in turn.

2.1 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, that is, the reaction:



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 - 250°C. The solubility of quartz at saturated water vapour pressure reaches a maximum at about 340°C in pure water. An equation valid for the quartz solubility from 20 to 340°C is given by Fournier (1986):

$$t = -42.196 + 0.28831 \cdot C - 3.6685 \cdot 10^{-4} \cdot C^2 + 3.1665 \cdot 10^{-7} \cdot C^3 + 77.034 \cdot \log C.$$

where t = Temperature in °C; and
 C = Silica concentration in mg/kg.

These relationships are, of course, the basis for the quartz geothermometer.

Quartz is also unusual in that there is an increase in solubility with pressure. However, the pressures required are large.

2.2 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:

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

where C and T have the same units 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. This defines a ‘window of opportunity’ where heat can be extracted from the brine without the possibility of silica scaling.

The solubility equations above 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. Figure 2 shows the relationship between the solubility of amorphous silica and temperature at different salt contents.

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).

2.3 pH dependence of silica solubility

Quartz has a crystal structure where every silicon atom is surrounded tetrahedrally 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:



Log K_1 (the first dissociation constant) for this reaction is given by:

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

Log K_1 at 100°C is -8.96, which means that at a pH of ~9.0, approximately 50% of the silica acid dissolved is present as the $H_3SiO_4^-$ ion. 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 3). As the pH is increased, further dissociation is possible to form $H_2SiO_4^{2-}$, however, these are only significant at very high pH ($\log K_2 = -11.0$ at 100°C).

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:



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

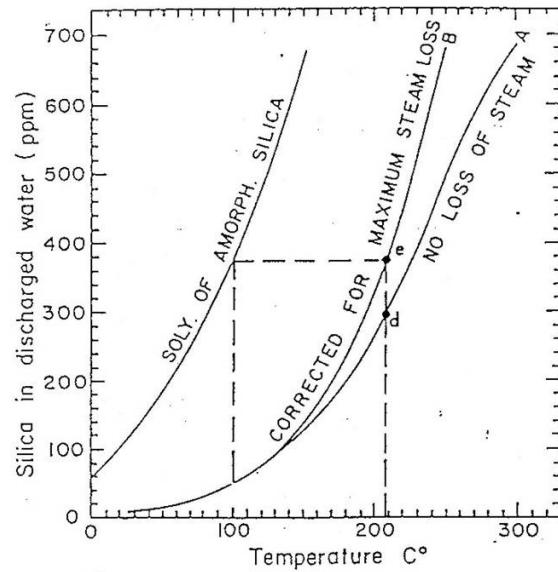


FIGURE 1: The solubility of quartz and amorphous silica with temperature
(from Truesdell, 1976)

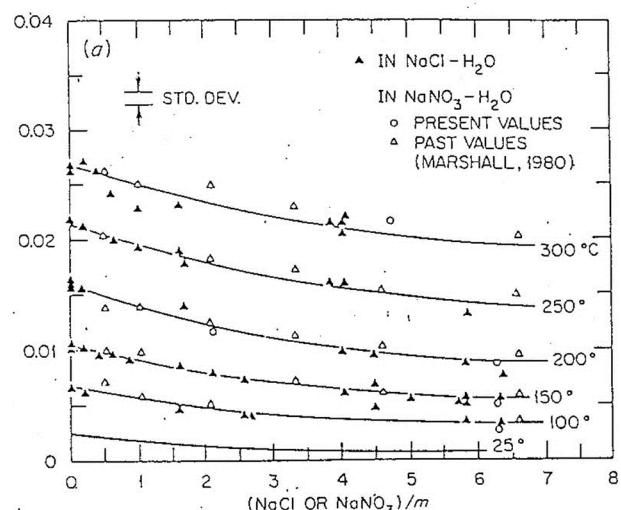


FIGURE 2: The solubility of amorphous silica in aqueous NaCl solutions
(Chen and Marshall, 1982)

$$S = C [1 + \{10^{pH} * K_1 / \gamma_{(H_3SiO_4^-)}\}]$$

where C = Solubility in mg/kg from Equation 1

K_1 = Dissociation constant above

$\gamma_{(H_3SiO_4^-)}$ = 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 3. 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 as the acidic gas is extracted from the brine. This then increases the solubility of amorphous silica.

This increase in amorphous silica solubility at Broadlands/Ohaaki allowed the reinjection temperature to be lowered to 155°C rather than ~ 175°C allowing a considerable increase in power production. The higher temperature is the amorphous silica solubility without the pH correction.

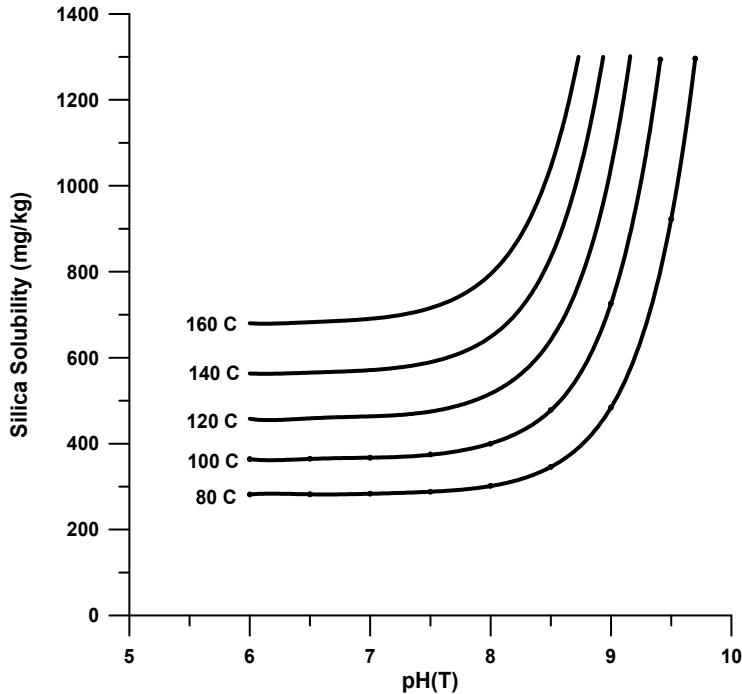


FIGURE 3: Calculated amorphous silica solubility for Br22 well ($I = 0.047$)

2.4 SST and SSI

The difference in solubility between quartz and amorphous silica allows exploitation of geothermal systems without the possibility of silica scaling. Although the deep fluid is probably saturated with respect to quartz, it is under-saturated with respect to amorphous silica. For a flash plant system, as the fluid undergoes adiabatic steam loss rising in the well and in the flash plant(s), there are two separate effects:

1. The concentration of silica in the separated water is increased by the effect of steam loss.
2. The 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 flash temperature at which the separated water just 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 in the separated brine.

For a pure binary system, there is adiabatic steam loss in the well followed by conductive heat loss in the binary system. In this case, the *silica saturation temperature* is normally defined as the temperature at which the brine exiting the heat exchangers just reaches saturation with respect to amorphous silica.

A 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 $\text{SSI} > 1.0$ then silica scaling is possible, if $\text{SSI} < 1.0$, then generally, silica scaling will not occur.

2.5 Kinetic aspects of silica deposition

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 thermodynamically 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 completely 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
7. Other unknown factors

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 can be a porous, low bulk density, sometimes not very adhesive, sometimes softer deposit, while the second tends to give a vitreous, very hard, difficult to remove, high density scale.

2.6 Colloids

Colloids are defined as small particles of a substance suspended in a 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 – 3000 nm. The particles are kept from settling with gravity by Brownian motion (which defines the upper limit of size). 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.

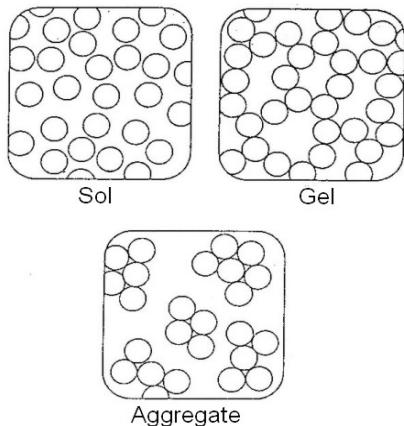


FIGURE 4: Forms of silica colloids

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 4).

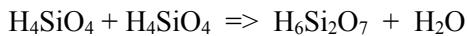
2.7 Silica colloid formation

As it is currently understood, the formation of the stable colloidal suspension takes place in three phases:

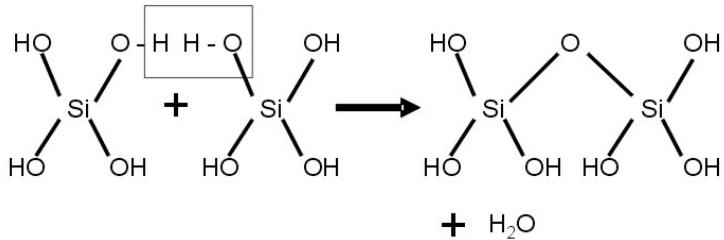
NUCLEATION, RIPENING and GROWTH.

Nucleation:

When two silicic acid molecules come together in a supersaturated solution they can combine to form a dimer $\text{H}_6\text{Si}_2\text{O}_7$ and a water molecule:



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 and is therefore amorphous. 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 (i.e. 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 (e.g. by further cooling) then the particles already formed can grow. Usually, no further particles are formed - i.e. 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 bond to an already formed particle. The final size of the colloidal particles can range from ~0.003 to 5 μm . Typical silica colloids are shown in Figure 5. Note that all the colloids are the same size.

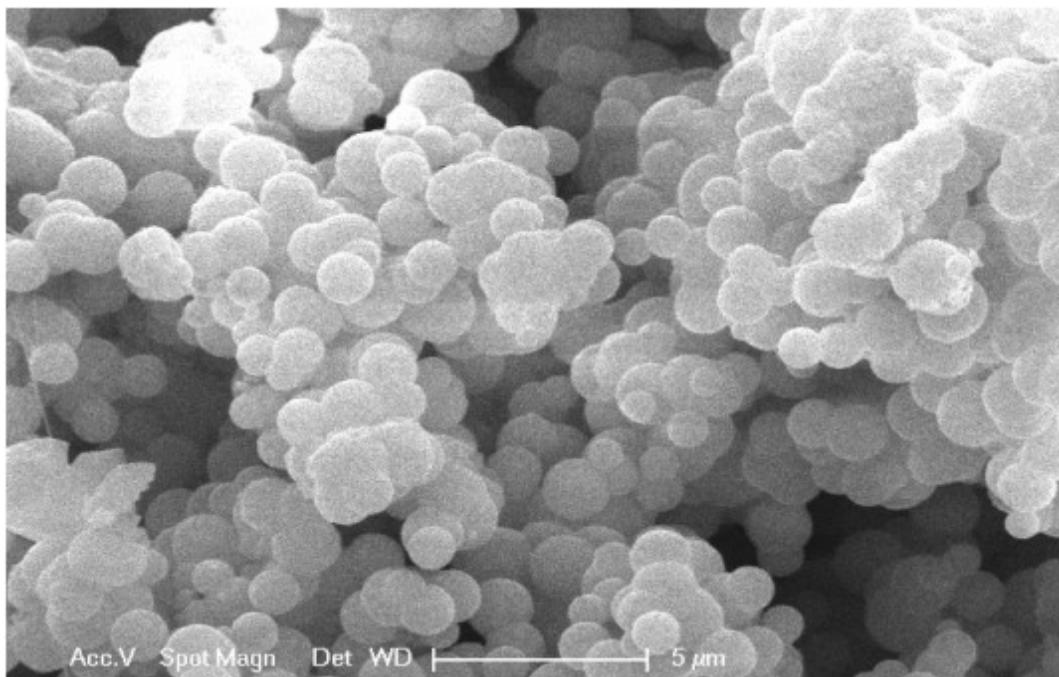


FIGURE 5: Typical silica colloids

2.8 Silica colloid properties

Individual silica colloids are spherical as shown in Figure 5. 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, then 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 nuclei are formed, and then excess silicic acid molecules grow the already formed particles, which leads to a smaller number of larger particles.

2.9 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.

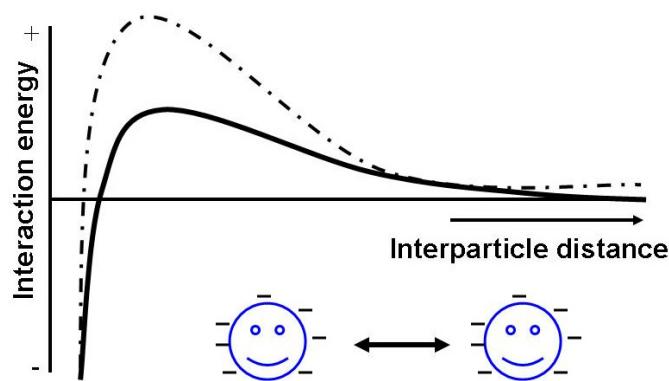


FIGURE 6: Colloid interaction with separation

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” chemical 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.

2.10 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’s negative surface charge 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 7. Rapid agglomeration leads to either rapid scaling, or in solution leads to gravity settling of the aggregated colloids as their size and molecular weight cannot be supported by Brownian motion.

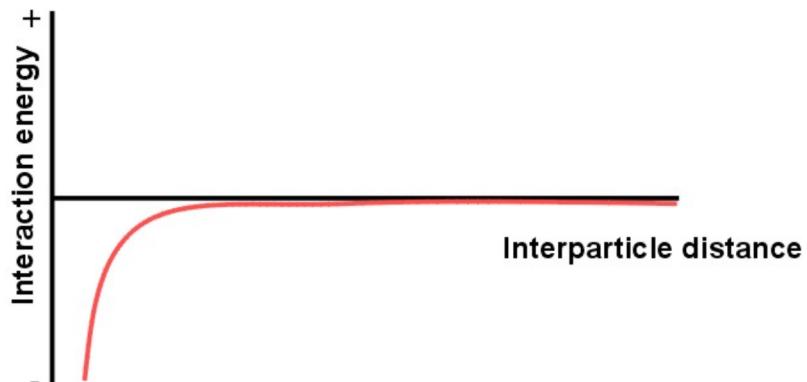


FIGURE 7: Colloid interaction in high ionic strength

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 list 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. Experience at Wairakei in the waste drains showed that Fe^{3+} greatly increased the deposition rate of silica. 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 co-deposited aluminium can also reduce the solubility of the amorphous silica formed (Gallup, 1977)

2.11 Effect of 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 8. In these experiments, three particle size colloids (120, 70 and 15 nm), and two fluid velocities (2.5 and 1 m/s) were exposed to the same total silica concentrations at the same temperature for the same time period. From the figure, it is obvious that the small particles cause very little silica scaling.



FIGURE 8: 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

Recent work by Kokhanenko et al. (2013) has linked the theoretical equations for particle transport in a fluid, with the DLVO theory. If the electrostatic interactions between particles are ignored, the rate of arrival of particles to the surface is several orders of magnitude greater than the observed scaling rate. If DLVO theory is included, however, the theory correctly predicts that only 1 in 10^4 to 1 in 10^6 arrivals results in attachment. Wall roughness is shown to increase the scaling rate significantly, as is observed in practice.

2.12 Measurement of silica polymerisation

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 9.

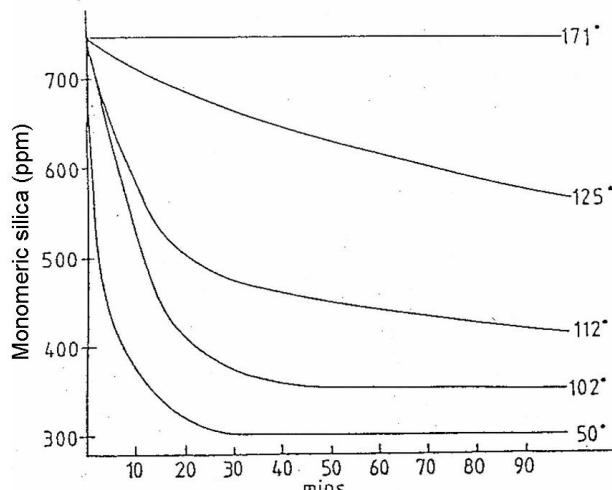


FIGURE 9: Rate of disappearance of monomeric silica as a function of time at different temperatures

It can be seen that at 171°C, 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 10. In this example, the silica polymerisation has been delayed at the lower pHs, while at the normal pH, silica polymerisation is very rapid.

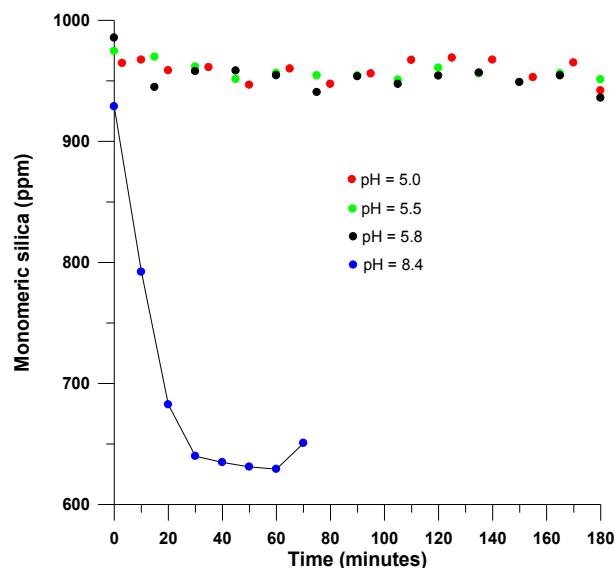


FIGURE 10: Silica polymerisation as a function of pH

2.13 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 over a period.

2.14 Treatments to cope with silica deposition

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.

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 under-saturated. 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.

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 (see later).

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 scaling rate due to the hydrodynamic effect.

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 6). There are currently a number of programs in progress to develop and test these ‘colloidal dispersants led by commercial interests.

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. Removal of silica colloids of a specific size and having specific surface properties can be very lucrative (US\$10/kg) and research is continuing in this area.

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 100°C 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. A possible side effect is the deposition of calcite, but this can be controlled by the addition of antiscalant.

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 Arnórsson (2005).

2.15 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.

3. ANTIMONY AND ARSENIC SULPHIDE SCALING

With the increasing demand for electricity, the use of binary generation for bottoming plants is increasing. As well, binary plants are receiving more attention for development of lower temperature resources and even for higher temperature resources where maintenance of reservoir fluid volume is important.

Geothermal reservoir fluids often contain small concentrations of antimony and normally greater, but still small concentrations of arsenic. Binary plants often have lower brine temperatures than conventional flash plants. Moreover, due to either pH modification, or addition of condensate, the brine can have low pH. Under these conditions, antimony (III) sulphide (stibnite) can precipitate in the heat exchangers and cause a loss of heat transfer and can eventually block the heat exchanger tubes.

Stibnite has also been observed in conventional flash plants where brine is subjected to pH modification followed by cooling to lower temperatures – for instance where cooled water is required for pH measurement.

Although arsenic sulphide has higher solubility than antimony sulphide, at low temperatures arsenic (III) sulphide can also precipitate and cause the same problems as stibnite.

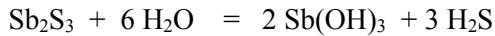
Re-evaluation of the thermodynamic data has led to more accurate data for stibnite equilibrium thermodynamics and has been verified in a geothermal binary plant.

3.1 Thermodynamics of antimony sulphide

Stibnite is antimony (III) sulphide Sb_2S_3 . It occurs naturally as a mineral that normally forms acicular (long, needle-like) black crystals. Like arsenic, antimony has two main oxidation states Sb^{3+} and Sb^{5+} . Thus stibnite has antimony in the reduced oxidation state of +3. Crystalline stibnite is soft (mohs hardness = 2), and has a density of 4.63 g/ml. The melting point is 550°C.

Sb_2S_3 also occurs as metastibnite. This is the amorphous analogue of crystalline stibnite. When stibnite is formed rapidly, for instance if a concentrated alkaline solution is acidified, then metastibnite is often formed. Metastibnite is an amorphous (non-crystalline) colloid and is red coloured.

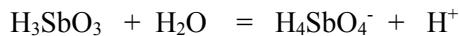
Stibnite dissolves in water to form the “hydroxide” $\text{Sb}(\text{OH})_3$ given by:



However, this “hydroxide” behaves more like an acid, so it is often written as H_3SbO_3 which is called antimonous acid. It can dissociate to form an anion (negatively charged species) according to:



which is sometimes also written as:



The species H_4SbO_4^- is also sometimes written as $\text{Sb}(\text{OH})_4^-$. The pK for this reaction is 12.04 at 25°C, which means that at a pH of ~ 12 at 25°C, there is approximately equal concentrations of H_3SbO_3 and H_2SbO_3^- . As the pH is increased, more of the H_3SbO_3 is converted to the anion. As the anion H_2SbO_3^- is charged, it has a very high solubility in water. This is the basis for adding caustic soda to dissolve the stibnite.

A number of other complexes of Sb(III) have been proposed that are also based on the antimony hydroxide such as $\text{Sb}(\text{OH})_2^+$ and $\text{Sb}(\text{OH})_2\text{F}$. Antimony does not occur as the free ion (Sb^{3+}) except in very acid conditions.

However, in solutions where H_2S is present, stibnite can also dissolve to form sulfosalts of antimony:



These ‘thioantimonites’ dissociate in alkaline solutions to form the anions of the thioantimonites:



and



These thioantimonites are only significant where the H_2S concentrations are significantly large or when the temperature is lower with H_2S present. They are, however, more stable than their arsenic analogues.

Antimony also exists in oxidised +5 forms. There is a slow oxidation in air for Sb (III) compounds and eventually the oxidised Sb (V) species is formed as $\text{Sb}(\text{OH})_6^-$. The effect of bacteria on this oxidation has not been studied. However, in geothermal brines, Sb (III) is the oxidation state.

Antimony also exists in a (-3) oxidation state in the gas stibine SbH_3 . This compound is extremely toxic and can be formed by the action of acid on antimony compounds in the presence of reducing compounds – like zinc. It has a similar smell to H_2S , so can be hard to detect in geothermal situations.

There is still some disagreement in the literature about the exact nature of all of the antimony complexes, and it is not currently a large area of research. Although there is a large amount of data on arsenic complexes, the literature is rather lean on antimony complexes.

3.2 Thermodynamics of arsenic sulphide

Arsenic is also present in geothermal brines as the reduced As (III) form. Like antimony, it does not occur as discrete As^{3+} ions in solution, but as H_3AsO_3 . Like antimony, this can also dissociate in alkaline solutions to form H_2AsO_3^- . The pK_1 and pK_2 for arsenites are 9.23 and 12.13 at 25°C, so the arsenious acid H_3AsO_3 is the stable species at normal geothermal pH.

Also, in a similar manner to antimony, arsenic in the presence of H_2S can form thioarsenites such as $\text{H}_3\text{As}_3\text{S}_6$, $\text{H}_2\text{As}_3\text{S}_6^-$ and $\text{HAs}_3\text{S}_6^{\equiv}$.

Arsenic also exists in an oxidised +5 state as arsenic acid H_3AsO_4 . The pKs for dissociation of arsenates are 2.2, 6.97 and 11.53 at 25°C, and so the species H_2AsO_4^- and HAsO_4^{\equiv} are the stable species at normal pH. Arsenic (III) is oxidised to As (V) slowly in air, but experiments in the Wairakei geothermal drains have shown that this reaction rate is significantly increased where bacteria are present.

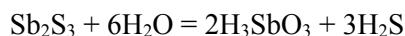
Arsenic also exists in a -3 oxidation state in the gas arsine AsH_3 . It is also very toxic.

3.3 Antimony sulphide in geothermal development

Antimony sulphide solubility is very sensitive to temperature and pH changes. The operation of some binary plants can encounter both lower pH and low temperature. Specifically, where steam is condensed in a vaporizer and then is added to the brine, and then led to a preheater, there is the opportunity for low

temperature and low pH. It is mainly under these conditions that stibnite has been deposited in binary plants in New Zealand.

Antimony concentrations in geothermal brine are typically less than the arsenic concentrations – sometimes an order of magnitude less. However, it is normally stibnite that is observed in binary plant preheaters. Typical antimony concentrations are < 1 ppm, but calculations show that it can be almost quantitatively deposited as stibnite. If we consider just the reaction:



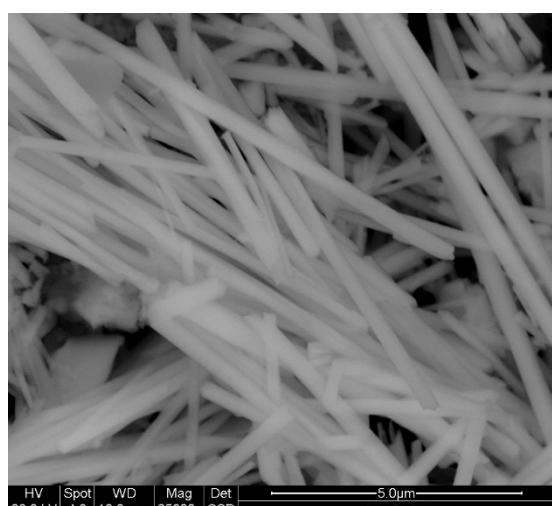
then calculations of the solubility of stibnite as ppm Sb as a function of pH, temperature and H₂S concentration are as follows:

	pH = 5	pH = 5	pH = 8	pH = 8
Temp. (°C)	5 ppm H₂S	15 ppm H₂S	5 ppm H₂S	15 ppm H₂S
25	6.50E-08	1.24E-08	2.51E-06	4.83E-07
50	4.91E-06	9.37E-07	4.32E-04	8.32E-05
100	7.97E-03	1.52E-03	1.01	0.19
150	3.34	0.637	224	43
200	446	85	9852	1897

As can be seen, there is a very large temperature effect, with stibnite solubility decreasing by 2 -3 orders of magnitude with a 50°C drop in temperature, and also a large pH effect with 2-3 orders of magnitude drop in solubility between pH = 8 and pH = 5.

The speciation of the antimony in solution is also affected by temperature and pH. As an example, a brine with H₂S = 10 ppm and Sb = 0.2 ppm has the following calculated speciation at different temperatures and pH. The speciation is given in ppb of contained Sb for comparison.

Temp. (°C)	pH	Sb(OH)₃	HSb₂S₄⁻
25	5	0.02	200
150	5	194	6.49
25	7	0.01	200
150	7	198	1.48
25	8	0.09	200
150	8	198	0.00



There are also very small amounts of other antimony species present.

In binary plants, the stibnite is precipitated usually as the black crystalline form, rather than the red amorphous form. The crystals are acicular – long thin needles (Figure 11). These needles pack loosely on the heat exchanger pipe surface and form a very porous layer that can trap brine. The needles, plus the trapped brine can reduce the heat transfer in the heat exchanger. As well, the silica in the brine that is trapped in the pore spaces can polymerise and deposit. This can change the scale from a soft, easily removed scale to one more difficult to remove mechanically.

FIGURE 11: SEM of stibnite crystals

Where the stibnite is precipitated quickly – for instance by acidifying a caustic solution, it deposits as the red amorphous compound (Figure 12).

Originally, it was thought that stibnite might be volatile and could precipitate in steam lines. However, no evidence has been found that stibnite is distributed into the vapour phase.

3.4 Stibnite mitigation in binary plants

A number of possibilities exist for mitigating the deposition of stibnite. However, some are either not practical or not economic options.

Avoidance of low temperature

If the brine temperature is maintained above the saturation temperature for stibnite, then deposition cannot occur. This is generally not a practical solution as there can be a considerable loss of power generation.

Avoidance of low pH

The low pH that occurs in binary plants is normally due to the low pH condensate being added to the neutral brine. If these two streams are kept separate, then stibnite deposition is normally unlikely to occur. The acidity in the condensate is due to dissolved gases. If these gases could be purged, then perhaps they could be mixed with brine prior to the preheater without causing stibnite deposition.

Caustic dosing

Either the condensate or the mixed brine could be dosed with caustic to raise the pH. The required pH can be calculated, but is normally not that high. However, caustic is expensive, and this method normally is not economically viable.

Chemical inhibition

It may be possible to develop an antiscalant in a similar manner to the use of calcite antiscalants. Some encouraging research has been carried out in this area, but as yet, there are no antiscalants on the market that have been shown to be successful in totally inhibiting stibnite deposition. However, research is continuing.

Mechanical removal

If no preventative measures appear to be practical, then periodic removal of the deposit becomes the only option. High pressure water blasting using specialist rotating tube cleaning heads was found to be partially successful, but found to be expensive, slow and messy. The latter is important as stibnite is a hazardous material.

Later, specialised water flushed drilling equipment was employed and this proved to be very effective but still very time consuming. The time factor is also important, as this is a loss of power production leading to an economic loss.

Chemical removal

This is the method that to date is employed most successfully in New Zealand (e.g. Dorrington and Brown, 2000). Hot caustic soda is recirculated through the heat exchangers and the stibnite is dissolved very quickly. If silica is co-precipitated, then it also tends to be dislodged, but not necessarily dissolved. Cleaning an individual machine can be accomplished relatively quickly – a few hours – and loss of



FIGURE 12: Amorphous antimony sulphide

production is minimized. It is advisable to carry out this cleaning regularly. If heat exchanger tubes become blocked, then the caustic solution cannot pass through and incomplete cleaning is observed.

A second possibility is to divert the brine from the heat exchangers and just pass steam through the vaporizer and then the preheater for a period of time. Without the brine, the stibnite slowly dissolves and can be led to reinjection. This method has the advantage that (possibly reduced) power production is possible during the cleaning.

3.5 Arsenic sulphide in geothermal development

Arsenic sulphide behaves in a similar manner to antimony sulphide. However, arsenic sulphide is less commonly observed, despite the fact that arsenic concentrations are normally a magnitude greater than antimony concentrations. Recent experiments have shown that an amorphous arsenic sulphide can be precipitated at low pH and very low temperature. Consequently, although arsenic behaves in a similar manner to antimony, the saturation temperature and pH seem to be lower.

3.6 Sampling for antimony and arsenic

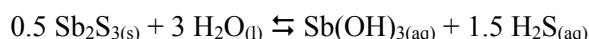
Traditionally, brine samples for antimony and arsenic analysis have been collected as filtered, acidified samples. However, the thermodynamics suggest that both arsenic and antimony would be better preserved in alkali. When this was tested on brine from a geothermal development, the following results were obtained. Concentrations of arsenic and antimony shown are in ppb:

	Preservative	Arsenic	Antimony
Accumulator	Acid	71	8
	Alkali	1850	426
Reinjection line	Acid	51	< 2
	Alkali	1230	165
Ultra pure water	Acid	< 10	< 2
	Alkali	< 10	< 2

From these results, it is clear that preservation with caustic is advisable for antimony and arsenic analysis. A further problem arises with the cooling coils used for sampling brine at > 100°C. If the residence time in the cooling coil is large, then stibnite can be deposited in the coil or stibnite crystals carried in the brine flow and then further analytical errors are seen. Consequently, it is sometimes quite difficult to obtain reproducible analyses for these elements.

3.7 Thermodynamic data

The thermodynamic data for the reaction:



have been investigated (Wilson et al., 2007). All the available data was critically analysed and revised equilibrium constants for the above reaction were obtained. The resultant line of best fit was:

$$\log K = -7640.3/T + 7.213$$

T = Absolute temperature in °K.

The use of these equilibrium constants agreed well with observed stibnite deposition at two geothermal fields.

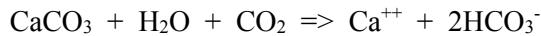
4. CALCITE SCALING

Calcite scaling can occur in geothermal production wells and occasionally in surface pipework and injection systems. It can rapidly reduce the flow in production wells to the point where they will no longer produce. It may form in the production well casing, or in some cases in the reservoir formation. When calcite forms in the reservoir, remediation is achieved by stimulating with acid cleaning. For the case where calcite would deposit in the well bore, it is possible to prevent calcite scaling by injection of antiscalant into the production well. This has become the preferred industry standard for mitigation of well bore calcite scaling. Remediation of scaled production wells is normally expensive, as it involves mobilisation and use of a drilling rig.

4.1 Background geochemistry

Calcite is calcium carbonate CaCO_3 . It is a common constituent in the rocks in geothermal areas. Geothermal waters interact with these rocks in the reservoir and dissolve some of the constituents until they come to chemical equilibrium. When the geothermal water is brought to the surface in a production well, the physical and chemical conditions change, and some of the rock constituents are no longer fully soluble, and these constituents can form a deposit. Calcite is in this category.

Geothermal fluids in the deep reservoir commonly contain dissolved carbon dioxide (CO_2) under pressure. This carbon dioxide can dissolve calcite in the rocks and convert it to soluble calcium ions (Ca^{++}) and bicarbonate ions (HCO_3^-) according to the chemical equation:



The greater the amount of CO_2 dissolved in the geothermal water, the greater the amount of calcite that can be dissolved. Calcite in the reservoir will dissolve in the geothermal liquid until a chemical equilibrium is reached.

When a single phase brine enters the production well, it rises up the well and the pressure decreases as the overlying hydrostatic pressure is reduced. At some point in the rise up the well, the hydrostatic pressure equals the saturated water vapour pressure plus the dissolved gas pressure, and the brine ‘boils’ to form a liquid water phase and a vapour (steam + gas) phase. At this point, a large proportion of the gas that was previously dissolved in the liquid is distributed into the vapour phase. When this CO_2 is lost to the liquid phase, the chemical reaction above is reversed:



Therefore at the level of boiling in the production well (the water level), calcite is precipitated. Unlike silica, there appears to be very little time delay between the calcite becoming oversaturated and it forming a deposit. The calcite is deposited as crystals on the casing walls (Figure 13). This decreases the internal diameter of the casing and thus the pressure drop across the point of scaling is increased. This in turn increases the amount of CO_2 lost to the vapour phase and more calcite is deposited at the point of pressure decrease.

FIGURE 13: Calcite scaling in a 3” bore. This deposit formed in ~ 3 weeks

Calcite is unusual in that it has retrograde solubility. This means that as the temperature is decreased, calcite becomes *more* soluble (for the same amount of CO₂ present). The effect of this for many geothermal wells is that as further boiling takes place as the geothermal two-phase mixture rises in the well, it reaches a point where the temperature has cooled sufficiently that no further calcite is deposited. Typically, calcite is seen to deposit on the casing over several hundred meters above the water level in the well, although in some wells with very high CO₂ concentrations, small amounts of calcite can still deposit at the surface. A typical calculated calcite deposition in production well casing is shown in Figure 14.

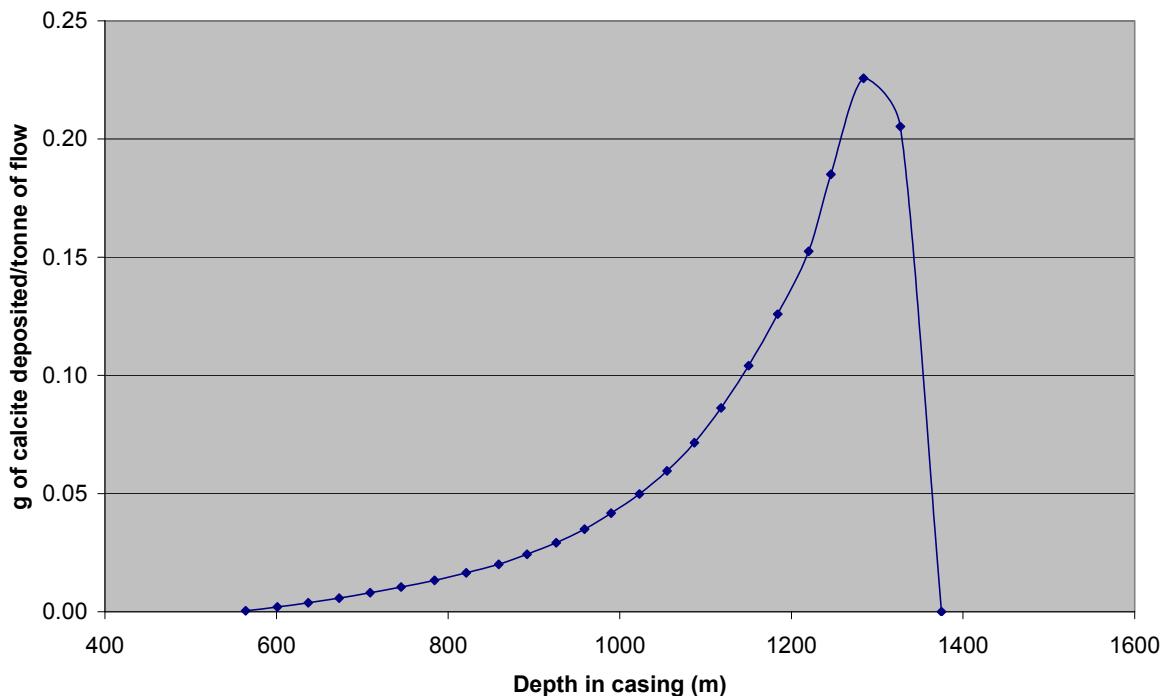


FIGURE 14: Typical calcite scaling profile in a production well

Normally, calcite scaling occurs in the production casing. However, if the well is run at very low well head pressures, or the reservoir is two-phase after extended drawdown, then the boiling zone of the geothermal liquid may not be in the well casing, but could be in the reservoir formation. If this occurs, then calcite deposition will occur in the formation and then become much more difficult to handle. In this case well productivity may be restored by stimulation with acid. A mixture of acids and corrosion inhibitors can be introduced at targeted depths using a coiled tube unit.

As the reservoir is produced with time, the gas content of the geothermal fluid in the reservoir is often depleted and calcite scaling can become less of a problem, and may disappear completely.

4.2 Calcite scaling mitigation

There are three basic methods for coping with calcite deposition. These are:

- Calcite antiscalants
- Mechanical removal
- Acidisation

The first two methods are useful where the scaling has occurred inside the production well casing. Acidisation is normally reserved for cases where calcite scaling has occurred outside the well casing in the reservoir formation.

4.3 Calcite antiscalants

Calcite antiscalants are compounds that interfere with the formation of the calcite crystals as calcite becomes oversaturated. These compounds restrict calcite formation by altering the surface of the growing crystal by attaching to small imperfections (crystal defects) in the crystal surface. Crystal growth normally takes place preferentially at these defects as the chemical energy is lower at these points. The antiscalants also react with the calcium ions (Ca^{++}) in solution (by chelation) to make them less available to form calcite. Typical antiscalants are polyacrylates, polymaleates, polycarboxylics, polyphosphonates and co-polymers or mixtures of these compounds. The particular mixture of these compounds depends on the chemistry of the brine. For low TDS brines, the fluids are reasonably benign and simple polyacrylates will probably suffice. These compounds are usually very effective at completely halting calcite deposition in production wells.

The antiscalant has to be present in the single phase geothermal brine before it loses the CO_2 at the boiling point – i.e. before calcite has started to form. Consequently, the antiscalant has to be introduced into the well casing below the water level for a flowing well. Typically, the dosing point is 100m or more below the measured water level. This allows for some drop in the water level with increased production. However, the dosing point will depend on the feed points into the well.

Where calcite scaling is occurring in the well casing, calcite antiscalants are the most common method of treatment in geothermal development around the world.

4.3.1 Practical aspects

The two most common failures in the antiscalant delivery system are fatigue failure of the capillary tube (breakage) and blockage of the tube.

Failure due to blockages is mitigated by limiting the residence time in the delivery system, using degassed condensate to dilute the antiscalant and implementing operational procedures to purge the capillary tube on shut-down.

A number of design solutions have been developed to mitigate the problem of fatigue failure. The early operation of Kawerau saw the use of $\frac{1}{4}$ " capillary tube with a sinker bar to maintain it in tension. Developments of this system included:

- Selection of inconel 825 as a material less susceptible to stress corrosion cracking and with good fatigue capability;
- Introduction of a stinger to protect the capillary tube from turbulent flow at the well-head;
- Armoured tube, to increase the tensile capacity of the inconel capillary and enable a larger sinker bar.

A similar system using capillary tube with a sinker bar is used in the Philippines, where it is reported that SS316 capillary tube is replaced annually.

For wells with higher productivity more robust antiscalant delivery systems have been developed. Dixie Valley employs a 1.9" hang-down string to protect the capillary tube for its complete length. Coso has developed a system using 1-1/4" coil tube to protect the capillary tube, this is introduced below the well head master valve. There is also a design proposed to use $\frac{3}{4}$ " tube to protect the capillary tube, which uses a hydraulically assisted winch rather than a more expensive coil tube unit.

Some antiscalants are acidic, as in polyacrylic acid. It is possible to purchase the neutralised form as the sodium salt and this is preferred.

Thermal stability is important, and when the antiscalant is selected, it is advisable to test the thermal stability performance with the NACE test. A high temperature/pressure laboratory is required to perform these experiments.

The raw antiscalant is usually around 30 – 50% of active product and can be quite viscous, so for ease of pumping in a dosing pump, the antiscalant is normally diluted. Dilution of the antiscalant also reduces the time spent in the capillary tubing at high temperature as it travels down the well and therefore reduces the risk of blocking and degradation. The antiscalant should be diluted with steam condensate from the plant that has been degassed. The degassing removes H₂S which can attack inconel. It is not advisable to dilute with town supply or river water, as these have high calcium and magnesium concentrations.

A typical installation has a central supply tank at the power station, together with a facility for condensate supply and mixing. The pumps are located at the station, and the antiscalant is pumped to the wellhead in capillary tubing attached to the two phase pipeline. This is a practical solution, as the antiscalant needs to be prevented from freezing.

The antiscalant needs to be filtered before it is pumped to the well, in order to reduce the occurrence of blockages. A very high pressure pump is also usually included in the circuit besides the dosing pump. This is used to clear blockages.

There has to be a graduated burette on the suction side of the dosing pump together with appropriate valving so that the dose rate of antiscalant can be verified. This should be checked daily.

The optimised dose rate of antiscalant is determined by experiment. A high dose rate – normally suggested by the supplier – is set on the dosing pumps and samples are taken at the surface and analysed for calcium concentrations. The dose rate is then reduced and further calcium concentrations are measured at the same point after a period to clear the well of the previous fluid. This process is repeated until low dose rates are achieved. The graph of calcium concentrations versus dose rate should show a plateau at higher dose rates, and then show a decrease in the calcium concentrations as the dose rate is decreased and calcite scaling is initialised in the well casing. The antiscalant dose rate is then set to the point where the calcium concentrations start decreasing, plus a safety allowance. This process takes about a day for each well. It is easier if analytical facilities for Ca are in-house.

4.3.2 Risks and drawbacks

If the tubing is introduced into the well vertically through the wellhead, then the master valve cannot be used. The side entry, as used at Coso, does permit the use of the master valve, but is a more complicated assembly and the design should be included as part of the well completion.

Consideration should be given to the required frequency of downhole well measurements. With such a capillary tube in the well, downhole measurements are no longer possible using conventional PTS instruments. Tubing must be removed first. The use of a hang-down string requires a well quench to remove it, whereas a coil tube based design may permit removal of the tube without quenching the well.

Care must be taken to ensure that if the antiscalant tubing becomes blocked, it is rapidly cleared. Otherwise the capillary tubing will become cemented into the well by the calcite scaling and can only be remediated with a drilling rig. This requires daily monitoring.

It has been noticed at more than one geothermal field where calcite antiscalants have been used, that a magnesium silicate scale has formed downstream in the brine at the surface at much lower temperatures.

Antiscalants cannot be easily used where the geothermal fluid is boiling in the formation away from the well casing.

4.3.3 Economics

Typical dose rates are 2 – 50 ppm (grams/tonne of brine) of the raw antiscalant. A simple polyacrylate costs about US\$3 - 5 per kilo and there are many similar products on the market.

An interesting innovation is available from some manufacturers. The antiscalant contains a fluorescent additive, which can be analysed using a fluorimeter at the surface as a check on the dosing rate. This can be automated and could provide low level alarms connected to the DCS, automatic adjustment of the dose rate etc., which could remove the human element from the dosing.

4.4 Mechanical removal

There are basically two methods available for mechanical removal of scale; milling and jet washing. If the calcite scaling is not too severe and is within the well casing, it is possible to produce from the wells, and then periodically cleanout the well casing to remove any deposited calcite when geothermal fluid production falls to unacceptable levels.

Milling is better suited to a rotary make-over rig, whereas jet washing could also use a coil tube unit. Jet washing can use water or be supplemented with acid.

The most significant impact of intermittent mechanical removal of scale is the loss of production, or the additional production, which needs to be maintained as a reserve. This mechanical removal requires mobilisation and use of a drilling rig or Coil Tube Unit to clean out the well casing. Depending on the position of the calcite scaling, there may also be a requirement to remove the slotted liner and clear the slots of deposited calcite. The cost of this solution can be improved by cleaning out multiple wells for a single mobilisation, but this has a negative impact on the requirement to have reserve production capacity.

In previous cases where this was used historically at Kawerau, production normally returned to flow rates close to pre-scaling values

In general, this is less cost effective than antiscalant, but if a well has been affected by calcite deposition, it is probably the only method of remediation.

4.4.1 Risks and drawbacks

A primary drawback is the expense of mobilising and using a drilling rig together with the loss of production.

There is always a small risk of some drilling failure where tools become lost or stuck in the well.

The cost of the lost production can be significant

4.5 Acidisation

This is normally only used where the calcite scaling is occurring in the formation away from the well casing. This is a specialised procedure, and requires specialised equipment provided mainly through petroleum based service companies. Calcite is dissolved by acid, and hydrochloric acid is normally used together with corrosion inhibitors. Although sulphuric acid is much cheaper, it forms and deposits anhydrite with the dissolved calcium, and is therefore not used.

The acidizing can be undertaken with a coiled tube unit. Normally feed zones would be selected separately for treatment and there is some argument whether top down or bottom up selection of the feed zones is preferable. Following the acidizing, the well is flushed then can return to production.

If measurements indicate that the reservoir liquid boiling has moved back into the reservoir formation, it may be possible to reduce production flow rates and shift the water level back into the well casing, where calcite deposition can much more easily be treated.

4.5.1 Risks and drawbacks

The use of acid requires specialised equipment and is a major exercise in OSH.

Where calcite deposition occurs in the formation, it will continue to deposit in the formation unless the well is produced with different WHP. Even then, if the reservoir is two phase, formation scaling may still occur.

The acidisation will always be more successful if the feed fractures are not completely blocked with calcite. Consequently, it is best not to wait until the well production has failed completely.

5. OTHER FORMS OF SCALING

Occasionally, heavy metal sulphide scaling has been observed in production wells. Significant quantities of these scales are most commonly seen in response to rapid pressure reduction of the brine, which results in loss of CO₂, H₂S, and pH changes (Brown, 1985, Hardardóttir et al., 2010, and others). Copper is often a major component, with minor amounts of zinc and lead present as sulphides. Quantities of precious metals are often associated with these scales.

Anhydrite (CaSO₄) scaling has also been observed in production wells. This probably results from the mixing of deeper, high calcium containing brines, with shallower sulphate-rich fluid.

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