



## SILICA POLYMERIZATION IN THE CERRO PRIETO GEOTHERMAL FIELD – A GENERAL REVIEW

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### ABSTRACT

An attempt to better understand the silica scaling problem in Cerro Prieto was made by reviewing publications regarding silica polymerization. It is expected that once the silica scaling problem is controlled, hot brine reinjection in Cerro Prieto can be achieved and the pressure drop effect in the reservoir can be minimized, as well as the influx of cooler groundwater. An increase in efficiency and productivity can also be achieved by avoiding adverse silica scale effects.

### 1. INTRODUCTION

Mexico has a total installed geothermal power generation capacity of 1008 MWe in four geothermal fields distributed around the country. The most important by size and production is Cerro Prieto (CP) geothermal field, located 32 km to the south of the USA border, near the city of Mexicali; the closest geothermal fields are Salton Sea, Geysers, Heber, East Mesa and Coso.

The field is divided into 4 exploitation zones named CP1, CP2, CP3 and CP4; almost all the wells located in CP1 have been abandoned due to a lack of pressure; the wells in CP2 are numbered 200's; the ones in CP3 are 300's and in CP4 are 400's. A new additional area was acquired last year to the east of the field and drilling in this part has already begun; the wells in the newer part are named 500's.

The brine from the wells enters a primary steam separator to produce high-pressure steam (12.4 bar-g); this first flashing moves most of the CO<sub>2</sub> and H<sub>2</sub>S into the steam phase allowing the pH from the residual brine to increase. The separated water goes into a secondary steam separator to produce low-pressure steam (5.2 bar-g); the remaining separated water is high silica scaling brine that is allowed to cool down in a pond to let the silica precipitate; some of this water evaporates and part is reinjected far from the reservoir. Only a small part of the separated water from the pond is reinjected inside of the reservoir, due to reservoir cooling provisions.

There are also four power plants, which do not necessarily receive steam from their respective exploitation zone. All the steam enters a steam-pipe net which distributes it to the power plants. Here is a brief description of each:

The first power plant, installed in 1973, was commissioned by the Toshiba company with a total capacity of 150 MWe generated by 4 condensing turbines of 37.5 MWe each with a consumption of 10 Ton/MW of single flash steam. An additional condensing unit of 30 MWe was installed later in 1985 for medium- and low-pressure steam of 12.5 Ton/MW.

The second power plant was installed in 1988, commissioned by the Toshiba company with a capacity of 220 MWe in two condensing turbines of 110 MWe each, with a total consumption of 9.5 Ton/MWe. These turbines work with high pressure in the first steps with an additional consumption of low steam pressure in the last steps.

The third was a twin power plant to the second and was commissioned by the same company.

The installed capacity in the fourth power plant is 100 MWe in 4 single flash turbines of 25 MWe each, high-pressure units, commissioned in the year 2000 by Mitsubishi Company.

### 1.1 Scaling problems in Cerro Prieto

In Cerro Prieto, the silica scaling problem has been an issue since the beginning of field exploitation. Many different approaches have been taken to minimize its impact from changing the pH to allowing the silica to precipitate in a pond. But no recent approach has been made to understand the mechanisms of silica polymerization and deposition.

There are no natural lakes or rivers flowing near Cerro Prieto that may feed the reservoir; the rainfall around the year is also very low. This is a main concern because, in the last years, the reservoir has been losing pressure, having more dry steam wells and lower pH which have brought casing corrosion problems; it is expected that a good reinjection program of the residual brine may minimize this impact. Field development politics urge an increase of the hot reinjection into the reservoir.

The problem with reinjecting hot residual brine is silica scaling during transportation and in the reinjecting wells. This residual brine may also be used to produce electricity in a binary power plant but the scaling problem remains.

A better understanding of the silica polymerization is needed to solve the mentioned problems in Cerro Prieto; this will help to increase generation and the overall efficiency of the thermodynamic cycle of the fluid.

In this report the information available regarding silica polymerization and scaling mechanism is reviewed as well as how it affects the efficiency in geothermal power plants. This will help to minimize the scaling impact in Cerro Prieto. Table 1 shows the average chemical composition of the separated brine in Cerro Prieto.

TABLE 1: Average chemical composition of the separated brine from Cerro Prieto

Parameter	Data
pH	7.74
Conductivity	38293 $\mu$ S/cm
SiO <sub>2</sub>	762 ppm
Ca	373 ppm
Cl	14258 ppm
Na	7723 ppm
K	1695 ppm

### 1.1.1 Well scaling

The reservoir in Cerro Prieto is liquid-dominated with sedimentary rocks at 300°C. From the moment the wells begin to flow there is scaling at the flashing point within the casing where the pressure drops allow silica to scale and clog the wells.

Once the well has scaled, it can be cleaned mechanically or chemically. The mechanical process needs a drilling rig to remove the scale using a drill bit with the same diameter as the inner diameter of casing where the scaling is experienced. The chemical process consists of adding acids such as HCl to remove the scaling; this may cause corrosion that will endanger the casing pipe within the well if the pH is not properly controlled.

There is an annual program in CP to mechanically repair wells but, since a well rig is needed, this increases the field maintenance cost.

### 1.1.2 Evaporation pond

The residual oversaturated brine, after separation from the geothermal wells, is sent by discharge channels to an evaporation pond (Figure 1).

The evaporation or oxidation pond is a 14 km<sup>2</sup> artificial pond originally made to remove minerals from the brine to produce fertilizers but, since its construction, it has been only used as a precipitation pond for silica precipitation. The water level of this pond has been increasing due to the silica deposition in the bottom. A dragging boat to remove this deposition must be acquired. A wave-breaker must be built to avoid water spillage during windy days. 8 deep well pumps and a screw pump feed the pond daily. All this has increased the maintenance cost of the geothermal field.



FIGURE 1: Higher water level in channels due to scaling

The brine follows a long path towards the evaporation pond to allow deposition and finally reaches the crystallizer ponds from which the cold and silica-free water is reinjected cold outside the reservoir in the northern part of the field.

### 1.1.3 Hot brine reinjection

Between 2006 and 2010, many attempts to reinject hot residual brine in Cerro Prieto have been made; a few examples are: well 303 which took the residual brine from two low-pressure wells in the zone known as CP1; well 626 in CP2 took the water from a nearby well to reinject it inside the reservoir. In both wells the reinjection was made by gravity with no pumping system or anti-scaler. Eventually, the pressure in the wells began to increase due to silica scaling inside the wells.

A prototype injection plant was developed 2010 to test the pumping system, wells and reservoir behaviour and to acquire the necessary experience in order to extrapolate from the results and reinject all the separated water and condensate from the turbines. This plant keeps the brine pressurized from 7 wells from CP3 in order to avoid scaling in the system and the wells. The brine is treated with commercial anti-scaling polymers in the 'christmas trees' of each well; the brine is reinjected into three wells, two of which inject directly into the CP1 reservoir and the other into the CP2 reservoir.

This model plant has given good results so far with no scaling in the system whatsoever, only a few technical problems. During this period of tests one of the wells died, thus reducing the brine in the system.



FIGURE 2: Seal damage due to scaling

#### 1.1.4 Turbine scaling

All of the 13 turbines installed in Cerro Prieto are of the backpressure type, with a total installed capacity of 720 MWe. Some of these turbines suffer iron silicate scaling, mostly in the last steps of the turbines (Figure 2), lowering the turbine efficiency; this has been minimized by a constant steam wash and a sporadic turbine wash, but this produces constant stress and wear in the system.

The scales found in the steam pipelines to the power plants are mainly magnetite and quartz with an average particle size of 200  $\mu\text{m}$ .

#### 1.1.5 Heat exchanger scaling

The water from the second separation still has appreciable enthalpy that may be used in a binary cycle system, but this residual brine is saturated and highly capable of scaling; once the brine gets into a heat exchanger, it will lose pressure and cool down, scaling the tubes. None of the commercial anti-scaling products tested have given good results in avoiding heat exchanger efficiency loss.

### 1.2 Scaling research in Cerro Prieto and Salton Sea

Cerro Prieto and Salton Sea geothermal fields have similar scaling characteristics, and many publications deal with this problem. In an attempt to analyse it, some of the most important papers have been reviewed.

#### 1.2.1 Cerro Prieto

The Cerro Prieto geothermal system is described as a water-dominated field with sedimentary and meta-sedimentary rocks (Lippman et al., 2002). Localized in the southern portion of the Salton Trough, it is an actively developing rift basin partially filled with sediments into which oceanic-type basaltic dikes are being emplaced. The field is in a tensional area developed between the ends of the right-stepping, strike-slip Cerro Prieto and Imperial faults. There are two reservoirs, the “Alpha” ( $\alpha$ ) a shallow reservoir (1600 m) in the west of the field and the “Beta” ( $\beta$ ) reservoir which extends over the entire field.

When a description of the Cerro Prieto reservoir was made by Ellis and Mahon in 1977 (Ellis and Mahon, 1977), only the CP1 zone was being exploited. Their description was that to the east the sedimentary strata was more compacted, and lower permeability was considered to be due to precipitation of calcite and silica in a zone of interaction between the hot fluids and a cold water front. An inflow of colder water at depths of 1000-2000 m caused cooler temperatures at deeper levels in wells on the eastern and western edges of the field (also in CP1). By that time, the salinity was 15000 – 17000 ppm total solids but still less than that found in Salton Sea field in Imperial Valley. The high

salinities, the authors suspected, were from the solution of evaporative sequences in the sediments filling the graben structure. The authors also reported high temperatures in the reservoir, up to 350°C.

A study was carried out on the precipitation of amorphous silica in (synthetic) Cerro Prieto brines at atmospheric pressure and 100°C, prior to reinjection (Weres and Tsao, 1981). The results of the study showed that the Cerro Prieto brine was supersaturated relative to amorphous silica by about threefold; the excess silica in solution was rapidly converting to suspended silica by homogenous nucleation and the growth of colloidal particles. The flocculation of this colloidal silica and its adhesion to solid surfaces created rock-hard, white amorphous silica deposition. Part of the dissolved silica quickly polymerized to form suspended colloidal silica, which flocculated and settled slowly at unmodified brine pH values near 7.35. Raising the pH to about 7.8 by adding base and stirring for a few minutes caused rapid and complete flocculation and settling. Increasing the pH destabilized the colloidal silica due to the higher negative charge on the surface of the particles with cations being adsorbed; the adsorbed cations served as bridges between the particles and this bridging effect caused the silica particles to adhere and flocculate. The flocculating ability of cations increased with their charge. In Cerro Prieto, calcium was the main flocculating ion at the time of the study. Quaternary commercial amines as flocculating agents seemed to be effective in some brine compositions.

The conclusions of the study indicated that the brine in CP should be aged for 10 minutes in a covered holding tank, 30 to 40 ppm lime ( $\text{Ca}(\text{OH})_2$ ) added, stirred for 5 minutes, and the flocculated silica separated using a clarifier. The brine should then be almost free of suspended solids. A decrease in pH could significantly reduce the scaling rate.

Weres and Tsao (1981) reported that the settling rates of colloidal silica in Cerro Prieto were relatively slow. The use of flocculants (lime and organic polymers) could accelerate the settling rate of colloidal silica. The Cerro Prieto hydrothermal brine type was reported to be alkali-chloride water, originating from a mixture of sea water and Colorado River water (see original paper for references). The calculation showed that hydrothermal fluid in CP1 was in chemical equilibrium with K-feldspar, Na-feldspar, Na-plagioclase, calcite, anhydrite, pyrite, pyrrhotite, graphite (coal) and possibly magnetite.

A similar process to the one described by Weres and Tsao (1981) was proposed (Hurtado et al., 1989) with a pilot plant description. To extend the reservoir life through thermal and hydraulic recharge, they proposed to reinject the disposal brine of high-concentration colloidal silica from the CP1 power plant, adding lime to the flashed brine and then aging it to obtain clarified brine with relatively low suspended solids. At atmospheric pressure, the brine was at 100°C and its silica solubility was less than 400 mg/l; in order to avoid silica deposition in the wellbore and reservoir, suspended silica must be removed prior to reinjection.

In research on Cerro Prieto conducted by Thomas and Gudmundsson (1989), the silica deposition rate was accelerated to reduce silicic acid concentrations to near saturation, thus preventing further deposition downstream; flashed brine was allowed to age and was then treated with lime and organic flocculating agents; after a period of settling in a clarifier, the brine was then suitable for reinjection into the reservoir formation.

In a study on the two reservoirs in CP1 by Portugal et al. (2006), a pH of 6.44 was obtained for the deep aquifer and 5.5 for the shallower one. In the northern part, the pH had lowered about 1.5 units since 1990, due to exploitation. The equilibrium between K and Na-feldspars and between K-feldspar and K-micas seemed to control the chemical composition of the fluids in both reservoirs. The primary minerals were quartz, feldspars, K-micas, ferromagnesian minerals and plagioclases. The main secondary minerals were K-feldspar, Na-smectite, Ca-smectite, illite, chlorite, quartz, calcite, pyrite, pyrrhotite, sphene, epidote, prehnite, actinolite, wairakite, biotite, iron oxides and vermiculite. Fluids in CP1 were oversaturated with respect to calcite, indicating calcite precipitation at reservoir conditions and in the injection well pipes. It is possible that calcite was precipitating around the well

in the formation where the reservoir was being recharged. According to the simulation, calcite precipitation started at 70°C.

DiPippo (2008) presented an actual overview on the Cerro Prieto field and power plants in his book and explained the steam thermodynamic cycle. The flash station, mentioned for delivering steam to unit 5, was removed and two flashing stations (north and south modules) in CP1 took the separated water from CP2 and CP3 wells to use the waste brine and the excess low-pressure steam to feed unit 5 after it was repowered in 2009. In the north module, a heat exchanger was installed to test different anti-scalers for future delivery of a binary power plant.

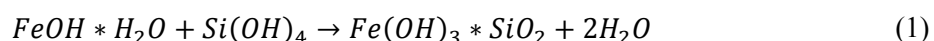
According to a previous work (Lippmann et al., 2002), by the year 2000, 115 million tons of fluids had been extracted from Cerro Prieto but only 20% had been reinjected back to the reservoir, producing a pressure drop, localized boiling and an influx of cooler groundwater.

### 1.2.2 Salton Sea

Silica with some iron oxide and lesser amounts of heavy metal sulphides was reported in Salton Sea (Harrar et al., 1978). An approach was proposed to stabilize the colloidal solids with organic compounds (such as polymers and surfactants) at 200°C. 49 substances were tested mixed with hyper saline brine (500 mg/kg) previously acidified to pH 4±0.3, and flashed to 1 bar at 100°C. 9 of these substances showed growth inhibition of the colloidal silica and produced an easily filterable mixture. The non-ionic materials proved to be the best surfactant type.

A report by Gallup (1989) indicated that iron silicate was the most prevalent scale deposited in the Salton Sea geothermal brine during processing to recover its heat content, where iron was being bound to silica through oxygen bridges. The scale appeared as brown-black, vitreous solids, resembling obsidian, at temperatures below 200°C. Primary ferric iron is chemically bound to silica in scale but, at low temperature (100°C), it is shown to consist of ferric and ferrous iron; there is more ferrous iron present at low temperatures. A crystallization-clarification process was developed to control this scale.

In the same report, epidote, pyrite, hematite and magnetite were described as potential mineral sources for ferric and ferrous iron in the brine. Iron in the brine is primarily present in the ferrous (+2) state as a result of reducing conditions provided by H<sub>2</sub>S. Iron silicate scale is believed to form by the reaction of hydrated ferric oxyhydroxide with monosilic acid or silicic acid oligomers as:



This occurs rapidly because ferric iron is known to have a strong affinity to silica. Fe(OH)<sub>3</sub> is predominantly used to coagulate many colloids in waste waters. Hydrolysed ferric iron is a known coagulant of silica dispersions. The hydrogen ions (H<sup>+</sup>), added during acidification, are believed to tie up the ferric oxyhydroxide and, thereby, inhibit the indicated reaction of ferric oxyhydroxide with silicic acid which forms insoluble iron rich silicates. By reducing the brine pH by ~0.3 units with hydrochloric acid, iron silicate scaling is controlled (Hoyer et al., 1997).

A previous work by Grassiani (1999) mentioned that the extent of silica depositions in Salton Sea resulted in the expensive solution of separating the silica before brine handling.

## 2. SILICA POLYMERIZATION AND SCALING

Much has been said about polymerization and many people associate it exclusively with plastics, but polymerization occurs in nature almost everywhere; an example is silica polymerization. This polymerization produces scaling, a well-known phenomenon in geothermal utilization.

Silica ( $\text{SiO}_2$ ) is a mineral frequently found in geothermal brine in amorphous and crystalline form.

## 2.1 Polymers

Polymers are defined (O dian, 1970) as macromolecules formed by the linking of large numbers of small molecules or monomers; this reaction, where monomers associate to form polymers, is called polymerization. As opposed to polymers, oligomers are molecules that consist of a few monomer units. Dimers, trimers and tetramers are oligomers.

## 2.2 Polymer classification

The silica polymerization would be classified (O dian, 1970) as an addition polymer and not a condensation polymer, because the structure of scaling is basically silica monomers (without the removal of any molecule) forming a long chain molecule. When the hot water from a well, saturated with silica, is allowed to flash by reducing its pressure, part of the liquid water evaporates leaving a more concentrated solution; thus, the remaining liquid water becomes supersaturated in silica that will tend to scale.

In another classification (O dian, 1970), silica was considered a chain polymer instead of a step polymer due to the mechanism of polymerization. The molecules in the silica polymer form full-sized polymer molecules almost immediately after the start of the first reaction; after the first molecules of silica have polymerized, grain nucleation and growth begin.

### 2.2.1 Silicic acid polymers

The concentration of silica found in “geothermal brines” is determined by the solubility curve of quartz and the temperature of the brine in the underground reservoir, because silica is generally present as quartz (Wahl, 1977). Silica concentrations are often used for estimating the downhole temperature by assuming that the brine is in equilibrium with quartz at the downhole temperature.

The basic structure of both silica and silicates is a tetrahedral arrangement of four oxygen atoms around one silicon atom (Wahl, 1977). The bonding between the silicon and oxygen atoms can be described as being part covalent and part ionic. The silicon atom in the tetrahedral structure is joined to four oxygen atoms by sharing one bond with each, thus producing a  $\text{SiO}_4^{4-}$  anion.

When monomeric silicic acid is formed in solution at a concentration exceeding the solubility of silica, two types of polymers are formed depending on pH (Matijevic, 1997):

1. At pH 2 to 3, chainlike or open-branched polymers are initially produced by condensation of silanol groups and can scarcely be considered as being “particles“ of  $\text{SiO}_2$ .
2. In an alkaline solution, polymers form followed by internal condensation and crosslinking, to give particles in which the interior consists essentially of silicon and oxygen atoms with hydroxyl groups attached to the silicon only on the outside.

It is likely that the larger the branched molecules initially form, the higher the pH and the longer the time required for rearrangement and internal condensation into dense, particulate polymers.

In acid solutions (Matijevic, 1997), these polymers have some temporary stability but, in neutral or basic solution they appear to rearrange almost instantly from the open-branched reactive form to spherical, dense silica particles, using the word “dense“ in the sense that inside the polymer unit there are few, if any, uncondensed  $\text{SiOH}$  groups. In the alkaline medium, the hydroxyl ion catalyses the

rearrangement of the polymer units to the most compact siloxane structure with only the silicon atoms at the exterior surface still bearing silanol groups.

In the pH range of 7 to 10 and with no more than about 0.2 N salt present, the colloidal particles adsorb hydroxyl ions and become charged so they mutually repel each other and do not aggregate. Since the polymerization produces branched polymers covering a range of molecular weights, each of these is converted to a corresponding silica particle by internal condensation so that a range of particle sizes is produced. Particle growth occurs rapidly under these conditions up to a particle size of around 5µm at ordinary temperature (Matijevic, 1997).

At low pH, silica particles bear essentially no charge (Matijevic 1997). Even in the pH range of 3 to 10, the potential is drastically reduced if an appreciable concentration of electrolytes is present. At low pH due to the absence of hydroxyl ions catalysing the transfer of silica, particle growth does not occur. On the other hand, even at low pH (down to pH 2), there are enough hydroxyl ions to promote the condensation of silanol groups to siloxane bonds. When two particles collide, Si-O-Si bonds form between particles through the condensation of the silanol groups, and the particles are irreversibly bonded together. Particles can be grown to different sizes and then aggregated by lowering the pH.

### 2.3 Scaling

Unlike calcite, which appears to precipitate soon after it reaches supersaturation, silica deposition is kinetically controlled and can be delayed after its saturation limit has been exceeded (Thomas and Gudmundsson, 1989). Siliceous scale is typically inert to most chemicals and, once deposited, is very resistant to mechanical removal. Hence, most treatment methods focus on the prevention of silica deposition or on controlling the morphology of the silica deposited.

In geothermal fields, silica polymerization is a serious problem and tends to occur when the temperature of brine is reduced with the dissolved silica starting to precipitate, the reactive centre being a cation, anion or a free radical. Polymerization occurs (O dian, 1970) by the propagation of the reactive species by the successive addition of a large number of monomer molecules through a chain reaction. If the temperature of the brine remains above the solubility limit, the silica will not polymerize (DiPippo, 2008).

Scaling can also occur when the pressure within the well-casing pipe drops below the critical point, flashing part of the fluid to steam; the silica content in this flashed fluid will remain on the pipe walls or in the formation. If flashing continues in the same zone, the resulting scaling will accumulate, reducing the flow area and producing a low-pressure zone uphill of the scaling and a high-pressure zone downhill, thus provoking more precipitation. In the downhill zone with a reduced scaled area, the flow velocity may increase and provoke vibration and noise. According to DiPippo (2008), at a certain wellhead pressure, further lowering of the pressure does not result in an increase in the flow rate as would be expected, and the flow becomes choked.

Once flashing occurs, the density is reduced and, thus, the velocity changes.

The growth of the polymer chain will cease when the pressure or temperature is moved to the critical point of silica precipitation solubility.

Changes in temperature and pressure disturb the equilibrium and generally lead to scale formation (Pátzay et al., 1998). A model was proposed to predict the bubble point (flashing within well), particle size evolution, scale formation, as well as saturation indexes. The non-condensable gases move into the vapour phase. The removal of CO<sub>2</sub> to a steam phase during flashing leads to calcite supersaturation, even though the accompanying temperature drop itself leads to calcite saturation increase. Since most reservoir fluids are close to saturation with calcite, carbonate scaling inside the



well above the bubble point depth and inside the production casing is a possibility for all geothermal wells.

Polymerization may also occur outside the well in brine pipes when a pressure drop within the mixture provokes flashing. That is why the pipe size must be big enough to avoid sudden pressure drops along the pipes and small enough to avoid small velocities that might produce silica precipitation. In Cerro Prieto, mixture pipes have been used to carry the brine to separation islands for more than 10 years, with a pressure of about 20.7 bar-g; only slight fouling has been encountered along pipes as long as 800 m. Also in Cerro Prieto, pressurized lines have been used to carry the high-pressure brine from the wellhead to the separator for about 400 m and at pressures above 55.2 bar-g.

### 2.3.1 Polymerization outside wells

Once the brine has left the wells, it is conducted to a separator to obtain dry steam; during this separation, the water supersaturates with silica content becoming highly scalable; this water can be wasted or re-separated to obtain lower pressure steam.

The increase in the concentration of solids due to flashing is determined by (Wahl, 1977):

$$\frac{W_F}{W_O} = \frac{1}{(1 - y)} \quad (2)$$

where  $W_F$  is the ratio of the concentration of the brine after flashing,  $W_O$  is the ratio of the concentration of the brine before flashing and  $y$  is the weight fraction of the flashed water.

The fractional weight change in composition,  $\Delta_w/W_O$ , (where  $\Delta_w$  equals  $W_O - W_F$ ) is derived from the equation above

$$\frac{\Delta_w}{W_O} = -y/(1 - y) \quad (3)$$

The other effect of flashing is the chemical change of the brine resulting from the removal of certain constituents such as carbon dioxide or hydrogen sulphide, changing the pH (Wahl, 1977). In addition, the indirect effect of flashing on the equilibrium as a result of temperature change is important in the chemistry of processes utilizing the geothermal brine.

### 2.3.2 Use of binary plants with silica scaling fluid

Double flash power plants are built when the reservoir exhibits high temperature (above 150°C). In such plants the amount of dissolved silica in the fluid medium will become higher than that in single flash plants (DiPippo, 2008). When the temperature of the reservoir is in this higher range, it is better to have backpressure units to ensure good turbine efficiency as the separated fluid (with enthalpy) can then be used as the heating fluid in a binary plant. While a binary plant does not flash the fluid, meaning there is no net increase of silica content as the fluid passes through the plant, the brine is already supersaturated coming from a secondary separation and is highly scaling. Also the pressure drop and cooling of the fluid in the temperature interchanger may induce scaling at that point.

The power range of the backpressure turbines is greater than that of the binary turbines: binary plants use turbines up to 10 MWe while backpressure plant turbines can be more than 100 MWe.

The heat exchanger of the binary power plant must not have “U” bends in the pipes in order to avoid scaling due to changes in flow velocity, and because bends are very difficult to clean.

A numerical method was proposed by Kubiak and Urquiza-Beltran to determine the thickness of the scaling on the blades of a geothermal turbine that decreased the output capacity and efficiency of the

turbine (Kubiak and Urquiza-Beltran, 2002); the change in the flow area was obtained by measuring the pressure before and after the first stage. According to their work, the power output decreased almost linearly with the steam pressure after the first stage and with the area's percentage decrease of the nozzle.

A previous work by Thomas and Gudmundsson (1989) mentioned that the periodic injection of deaerated water upstream from the turbine inlet nozzles was able to remove scale from the nozzles and the turbine blades. This has been done with excellent results in the geothermal fields of Cerro Prieto and Los Azufres, Mexico.

Metal sulphide and oxide scale deposition has been reported from almost all geothermal systems (Thomas and Gudmundsson, 1989), either directly from the geothermal brine or due to corrosion in the casing reacting with the sulphide. Metal silicates in Cerro Prieto form predominantly downhole in the flash zone. The rate of metal sulphide/oxide deposition is controlled by the degree of pH change during flashing and by the concentration of metal ions; the latter limits the rate of deposition of metal sulphides in high-temperature systems but, at high salinities, metal ion concentrations can be quite high, resulting in rapid rates of scaling. Grassiani (1999) mentioned iron carbonate and iron sulphide scales at East Mesa.

## 2.4 Amorphous silica

Amorphous silica (silicon dioxide)  $\text{SiO}_2$  does not have a crystalline structure as defined by X-ray diffraction measurements (Kirk and Othmer, 1979). It can be surface-hydrated or anhydrous. A silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atoms. Each of the four oxygen atoms is covalently bonded to at least one silicon atom to form either a siloxane (-Si-O-Si) or a silanol (-Si-O-H). The bond distances and bond angles are similar to those of cristobalite. A random arrangement of rings leads to the formation of complex structures of generally spherical particles less than 100 nm in diameter. These particles have high surface area values, generally greater than  $\sim 3 \text{ m}^2/\text{g}$ . There is a general absence of definitive lines in the diffraction patterns of silica when X-ray diffraction is used to determine the crystallinity of amorphous silica.

The  $\text{SiO}_2$  form of silica commonly shares the corners to link the coordination polyhedral, but sharing the faces never occurs due to the decrease in stability that would result from the close distance between silicon cations. Each unshared oxygen atom contributes to a formal negative charge to the anionic group thus formed, which is satisfied by the presence of other cations in the silicate structure.

There exist six structural types of silica, presented in Table 2.

TABLE 2: Forms of silica

Name	Structure	Shared atoms
Neso-silicate	Discrete ( $\text{SiO}_4$ ) units	No shared O-atoms
Soro-silicate	Discrete ( $\text{Si}_2\text{O}_7$ ) units	One shared O-atom
Cyclo-silicate	Closed rings	Two shared O-atoms
Ino-silicate	Chains	Two shared O-atoms
Phyllo-silicate	Layers	Three shared O-atoms
Tecto-silicate	Three-dimensional networks	Four shared O-atoms

Amorphous silica is distinguished by chemical composition, physical properties, and the characteristics of the particles (Kirk and Othmer, 1979). The most important chemical information is the amount of silica, %  $\text{SiO}_2$ ; percentage of associated water, total content of nonoxidizable materials, the presence of stabilizers, carbon content, the level of soluble salts, the level of nonsiliceous ash, the level of metal impurities and the silanol group density. Physical characteristics include pH, density

and tamped density, viscosity, turbidity, refractive index, light scattering properties, and/or the sedimentation rate.

There are different methods to characterize the morphology of silica (Kirk and Othmer, 1979); these are:

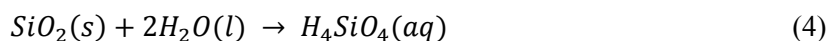
1. Specific surface: where the Brunauer-Emmett-Teller (BET) adsorption method is used to provide the sum of the outer geometrical surface and the inner surface (pores).
2. CTAB surface area: This method is based on the adsorption of surface active molecules from aqueous solutions to obtain the outer geometrical surface only.
3. Pore volume and pore size distribution: The most common methods to determine pore volume are mercury porosimetry and the BJH method.
4. DBP number, oil absorption: Provides an indication of the total volume of the liquid that can be absorbed by a silica sample.
5. Microscopic methods: Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) allow direct insight into the dimensions of interest, which provides information on the size of primary particles, aggregates or agglomerates and particle size distribution.

#### 2.4.1 Colloidal silica

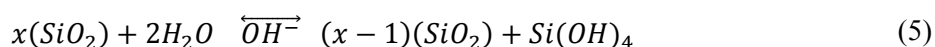
Colloidal silica is described as a stable dispersion or sols of discrete particles of amorphous silica (Matijevic, 1997).

### 2.5 Solubility

Amorphous silica dissolves or depolymerizes in water according to (Kirk and Othmer, 1979):



$\text{H}_4\text{SiO}_4(aq)$ , which is either a monosilicic or an orthosilicic acid, is also expressed as  $\text{Si}(\text{OH})_4(aq)$  or metasilicic acid  $\text{H}_2\text{SiO}_3(aq)$ . As described (Chan, 1989; Matijevic, 1997; Sheikholeslami et al., 2001), when solid phases of silica are in contact with water, small amounts of silica will dissolve and enter the aqueous phase. The dissolution of silica is governed by two chemical reactions: hydration and dehydration, which are catalysed by  $\text{OH}^-$  ions:

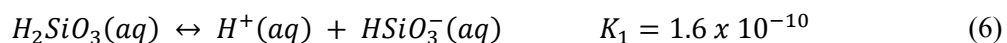


Hydration yields a soluble monomeric silica,  $\text{Si}(\text{OH})_4$ , which is also termed dissolved monomeric silicic acid. The solubility of amorphous silica in aqueous solutions is affected by temperature, pH, pressure and salt content. Raising the pressure increases the solubility of silica but is less significant than the temperature effect. The solubility of amorphous silica increases with increasing temperature and pH. Solubility of amorphous silica is highly affected by the presence of dissolved salts.

The solubility of amorphous silica in water at 25°C ranges from 70 to 150 ppm  $\text{SiO}_2$  (1.2-2.2 mmol/kg) (Kirk and Othmer, 1979). The variation results from differences in particle size, degree of hydration, and level of trace impurities. Areas having a small positive radius of curvature (convex) dissolve most extensively, and areas having a small negative radius of curvature (concave) dissolve least extensively. Particles having a diameter less than ~5 nm have a progressively greater solubility than do particles of continually increasing diameters. Particles <3 nm in diameter are very soluble.

Hydrated amorphous silica dissolves more rapidly than anhydrous amorphous silica. The solubility in neutral dilute aqueous salt solutions is only slightly less than in pure water. The presence of dissolved salts increases the rate of dissolution in neutral solution. Trace amounts of impurities, especially

aluminium or iron, cause a decrease in solubility. Acid cleaning of impure silica to remove metal ions increases solubility. The dissolution of amorphous silica is significantly accelerated by hydroxyl ions at high pH values and by hydrofluoric acid at low pH values. Dissolution follows the first order of kinetic behaviour and is dependent on the equilibrium shown in the following equations:



where  $K_1$  and  $K_2$  are the acid dissociation constants of silicic acid.

Above a pH value of 9, the solubility of amorphous silica increases due to increased ionization of monosilicic acid (Kirk and Othmer, 1979); the point of solubility at pH 8 was also mentioned (Sheikholeslami et al., 2001).

Kirk and Othmer (1979) also stated that dissolved silica undergoes polymerization to give discrete particles which can react further. The three stages of reaction are polymerization of monomers to form particles, growth of particles, and linking of particles to form chains and then networks. In basic solution, the particles grow in size and decrease in number. In acid solution or in the presence of flocculating salts, particles aggregate into three-dimensional (3D) networks and form gels.

At concentrations below ~100 ppm of  $SiO_2$  (Kirk and Othmer, 1979), the solubility of amorphous silica in water is such that monosilic acid is in true solution in the water. Polymerization occurs only when solubility is exceeded and there is no solid phase present on which the silica can be deposited. The polymerization is an ionic reaction proportional to the concentration of the hydroxyl (OH) ion at  $pH > 2$ . Because of the thermodynamic tendency to maximize siloxane, -Si-O-Si-, and to minimize silanol (-Si-O-H) bonds, initially formed low molecular weight species are condensed, forming ring structures, such as cyclic tetramer, hexamer and octamer. These species continue to react with additional monomers and become linked to one another. Internal condensation reactions continue to occur that lead to the formation of small particles. At temperatures  $> 80^\circ C$  and pH values  $> 7$ , the particles are anhydrous. The silanol groups generally only remain at the surface. These particles serve as nuclei upon which 3D particle growth occurs. Because of the solubility differences, small particles dissolve and the silica is deposited on larger particles that grow into average size. Increasing temperature either increases the growth of sol particles or causes gel formation. The presence of dissolved salts assists in neutralizing particle surface charges to enhance aggregation of the particles into 3D gels. The rate of aggregation also increases with dissolved silica concentration in solution. As polymerization occurs, the solution still contains dissolved silica at a concentration equivalent to the solubility of amorphous silica.

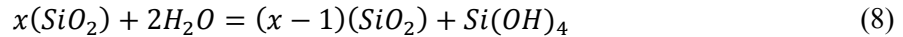
The temperature dependent dissolution and precipitation of silica may greatly affect porosity and permeability in a wide range of crustal rocks (Carrol et al., 1998).

There are three facts on solubility of amorphous silica (Matijevic, 1997):

1. Amorphous silica is involved in the colloidal silica-water system.
2. Amorphous silica is soluble in water to the extent of about 0.01%, expressed as  $SiO_2$ . The solubility increases with diminishing particle size, particularly below 5  $\mu m$ .
3. The soluble form of silica is the monomeric  $Si(OH)_4$  which is characterized by its rapid reaction with molybdic acid to form the yellow silicomolybdate ion.

It is a non-ionic material (Matijevic, 1997) which polymerizes rapidly if concentrations exceed a few hundredths of a per cent. The reaction is extremely slow at pH 1.5 but from 3 to 9 the rate increases in proportion to the hydroxyl ion concentration, whereas the saturation concentration of  $Si(OH)_4$  remains constant. From pH from 9 to 10.7, there is an apparent increase in the solubility of amorphous silica

due to the formation of silicate ions in addition to monomers which are in equilibrium with the solid phase. Since the silicate ions are instantly converted to monomers in acid solution, both monomer and silicate ions are included in the determination of “soluble silica” by the molybdate reagent. In this range, amorphous silica is in solubility equilibrium with neutral monomers as well as silicate ions:



Above pH 10.7, all the solid phases of amorphous silica dissolve to form soluble silicates, since at higher pH the concentrations of  $\text{Si}(\text{OH})_4$  are greatly lowered by conversion to ionic species, so that no amorphous solids can remain in equilibrium. The rate at which silica reaches solubility equilibrium depends not only on the pH and area of the silica exposed per unit volume of water, but also is strongly affected by Al and Fe, adsorbed on the surface.

### 2.5.1 Particle size

In all silica sols the particles are in solubility equilibrium with dissolved silica (Matijevic, 1997); small silica particles are more soluble than larger ones, so spontaneous growth of larger particles occurs at the expense of the smaller particles, even at ordinary temperatures.

The solubility of amorphous silica depends, from a thermodynamic standpoint, on the radius of curvature of the particular surface area of silica under consideration (Matijevic, 1997). The radius of curvature is generally considered positive, since particles are usually under consideration. Negative values of radius of curvature (crevices or holes) must be considered. The solubility in these regions must be less than that of the normal solubility of the flat surface or particle of infinite size.

There are two important practical consequences (Matijevic, 1997):

1. When very small individual silica particles are brought into the same solution as larger ones, especially at pH 9 to 10 where hydroxyl ions catalyse the dissolution and deposition of silica, the smaller ones dissolve and the larger ones grow.
2. If there has been an aggregation or flocculation of colloidal silica particles, so that two or more particles are brought together then, at the point of contact, the radius of curvature is negative and extremely small, the solubility of silica in this region is very low, and silica dissolves from the particle surfaces and is deposited around the point of contact to minimize the negative radius of curvature, thus forming a coalescence or neck between particles. At low pH the same phenomenon occurs if the silica particles are less than about  $5\mu\text{m}$  in diameter, where solubility changes rapidly with the radius of curvature.

Particles can be grown in a pH range of about 7-10, preferably around 9; spontaneous growth of particles occurs at a rate depending upon time, pH and temperature (Matijevic, 1997).

When a sol is gelled, it first becomes viscous and then develops rigidity; when a sol is coagulated or flocculated, a precipitate is formed (Matijevic, 1997). Also, aggregation includes:

1. Gelling, where particles are linked together in branched chains that fill the whole volume of sol so that there is no increase in the concentration of silica in any macroscopic region in the medium. Instead, the overall medium becomes viscous and then is solidified by a coherent network of particles which, by capillary action, retains the liquid.
2. Coagulation, where the particles come together into relatively closely packed clumps in which the silica is more concentrated than in the original sol, so the coagulate settles as a relatively dense precipitate (difficult to remove by filtration).
3. Flocculation, where the particles are linked together by bridges of the flocculation agent, which are sufficiently long that the aggregated structure remains open and voluminous (having pores which permit easy filtration).

4. Coacervation, in which the silica particles are surrounded by an adsorbed layer of material which makes the particles less hydrophilic, but does not form bridges between particles. The particles aggregate as a concentrated liquid phase immiscible with the aqueous phase.

Smaller particles of silica tend to form at lower pH and temperature; the strong effect of temperature on the surface area is explainable in terms of the effect of the supersaturation ratio on the nucleation phenomena at the start of polymerization (Thórdarson and Tómasson, 1989).

## 2.6 Induction period

An incubation or induction period is a major prerequisite to colloidal amorphous silica generation and further massive deposition (Grassiani, 1999). Induction periods may vary from several minutes to several hours and, in many cases, are long enough to permit normal flow and heat transfer inside the critical heat exchanger part of the binary plant.

## 2.7 Supersaturation

Silica concentration is determined by the equilibrium solubility of quartz in hot reservoirs (Chan, 1989). Nearly all dissolved silica is in monomeric form. The precipitation of silica is dominated by the solubility of amorphous silica. Depending on the degree of supersaturation, the dissolved monomeric silica may nucleate, form polymers, and deposit as amorphous silica.

The idea of a second flashing, in order to produce lower pressure steam, results in higher supersaturation values due to further concentration of the brine. Additionally, a certain rise of pH may occur, as some still dissolved acidic gases are released by the pressure drop; all of which boosts polymerization faster than if the brine was cooled without flashing (Grassiani, 1999).

The silica index (Grassini, 1999) is the actual concentration in ratio to the supersaturation concentration ratio.

The synthesis of colloidal silica in geothermal brine initially occurs when silica enters the brine, together with other compounds, as a result of a chemical reaction between water and aluminosilicate minerals in rocks of geothermal deposits at depth in a zone of thermal anomalies at elevated temperatures and pressures (Potapov, 2004). At 250 – 300°C, silicon in the brine appears mainly as individual molecules of silicic acid  $\text{H}_4\text{SiO}_4$ . Under these conditions, the total concentration  $C_t$  of silica  $\text{SiO}_2$  can be estimated from quartz solubility in pure water at 250 – 300°C:  $C_t = 500 - 700$  mg/kg. As the brine flows, its pressure and temperature decrease and the brine partially evaporates. The total concentration  $C_t$  of silica in water amounts to 700 – 1000 mg/kg and more. The aqueous brine becomes supersaturated with silica. The water solubility of silica depends on temperature.

The state of amorphous silica in the supersaturated aqueous brine is unstable (Potapov, 2004). The brine supersaturation, which is the difference between amorphous silica concentration and solubility, is the driving force for the nucleation and polymerization of silicic acid molecules, which are accompanied by the formation of siloxane bonds and partial dehydration.

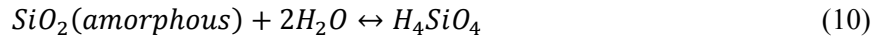
## 2.8 Precipitation rate

Silica particles tend to polymerize and precipitate at a certain rate that is affected by many factors such as silica concentration, particle surface and size, charges, temperature and pH until a certain equilibrium is reached.

### 2.8.1 Polymerization rate/kinetics

It was proposed (Wahl, 1977) that the rate of ionic reactions is instantaneous, as far as the reaction itself is concerned, because there is little or no energy barrier that must be overcome to form a precipitate once the ions are in proximity to one another. The reactions of solid salts to form ions in solution are limited by the rate at which the ions from the crystal can diffuse into the solution. The reverse reaction is limited by the rate at which the ions collide to form a crystal in the solution. Thus, all the reactions that take place in the geothermal brine will occur, essentially, instantaneously provided there is sufficient concentration of the material required for the reaction. An exception to this is the reaction of silica with itself to form higher polymers of silicic acid. This reaction can be very slow to occur, depending on temperature and pH conditions.

Silica polymerization can occur when the concentration of monosilicic acid in aqueous solution exceeds the solubility limit of amorphous silica (Chan, 1989). Excess monomers in the solution gradually disappear to form polymers. Dissolution/precipitation rates are dependent on reaction affinity (Carroll et. al., 1998):



where precipitation occurs on the left side of the reaction and dissolution on the right side.

The rate equation to describe the monomeric silica disappearance in solution is:

$$-\frac{dC}{dt} = k(C - C_e)^n \quad (11)$$

where  $C$  is the actual monomer concentration present,  $C_e$  is the monomer equilibrium concentration at the reaction temperature,  $k$  is reaction constant (according to Potapov (2004),  $k$  depends on temperature, pH and the ionic strength of the brine) and  $n$  is the reaction order. Polymerization of silicic acid to polymeric molecules is affected by pH, temperature, supersaturation, and salinity caused by the presence of other substances.

The reaction rate of silicic acids depends strongly on pH (pH = 6-10). In slightly alkaline or neutral solutions, polymerization is catalysed by hydroxyl ions. In very alkaline solutions, above pH 9, the reaction rate decreases. In highly acidic solutions, below pH 3, the reaction at room temperature appears to be catalysed by  $\text{H}^+$ .

The Gibbs free energy of reaction is:

$$\Delta G = RT \ln \frac{Q}{K_{eq}} \quad (12)$$

Solution saturation is equal to the ratio of the aqueous ion activity quotient,  $Q$ , to amorphous silica solubility constant,  $K_{eq}$ , assuming ideal unit activity of the solid phase.

A generalized equation describing the surface-reaction controlled precipitation rate, as a function of reaction affinity, is:

$$\text{Rate}_{ppt} = -\frac{d[\text{Si}]}{dt} = -K_{ppt} \left[ 1 - n \exp\left(\frac{\Delta G_r}{RT}\right) \right]^m \quad (13)$$

where  $K_{ppt}$  is a rate constant that may be dependent on the temperature, pressure, total reactive surface area, surface defect density, and any unidentified effect of the solution composition, and  $n$  and  $m$  are empirical constants. The form of the Gibbs free energy function,  $f(\Delta G_r)$  and its reaction order are used to infer the rate controlling mechanism for theoretical considerations.

It is difficult to distinguish between surface defect and the surface nucleation mechanism, because the form of  $f(\Delta G_r)$  and the reaction order effectively mask several important, yet non-measurable parameters, such as density, size and geometry of nucleation clusters, edge or step free energy and absorption frequency (Carrol et al., 1998). Precipitation rates controlled by aqueous diffusion to the mineral-solution interface are also linearly dependent on  $f(\Delta G_r)$ . Amorphous silica precipitation rates are dependent on reaction affinity, pH, and temperature. Amorphous silica precipitation rates increase with decreasing temperature because the geothermal waters are more supersaturated at lower temperature (for near constant silica input).

It was found by Carrol et al. (1998) that amorphous silica precipitation rates may be controlled by elementary reactions at steady state in solutions supersaturated by a factor  $< 1.3$ , supported by the linear dependence of the precipitation rate on  $f(\Delta G_r)$  in laboratory experiments.

It was also concluded by Carrol et al. (1998) that the amorphous silica precipitation mechanism is controlled by surface defect/surface nucleation processes and not by aqueous diffusion or rate limiting elementary reactions at the solid-solution interface in more supersaturated and chemically complex solutions. Amorphous silica precipitation then has a non-linear dependence on  $f(\Delta G_r)$ . If polymeric deposition occurs, then polymeric species form more readily at the mineral-solution interface than they do in the bulk solution.

Aluminium modifies the growth of silica polymers and decreases silica solubility; this was also described by Chan (1989). Matijevic (1997) also mentioned Fe. Yet another work (Sheikholeslami et al., 2001) mentioned that polyvalent metal hydroxides such as  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$  and  $\text{Mg}(\text{OH})_2$  are effective in removing both soluble and colloidal silica by precipitation; the addition of salts lowers amorphous silica solubility but, in addition, the alkaline environment favours the formation of silicate ions reacting with metal ions, forming insoluble metal silicates.

Rate expressions were presented (Icopini et al., 2005) that describe the oligomerization of silica in terms of the initial silica concentrations, ionic strength, and pH for a natural brine solution. The oligomerization rate increases as pH approaches near neutrality and as ionic strength increases. At ambient temperature, the process begins with the condensation of monosilicic acid to form disilicic acid and continues with monomer additions to form trisilicic acid and tetrasilicic acid. The oligomerization proceeds to minimize the abundance of uncondensed  $\text{Si}(\text{OH})$  bonds in favour of more condensed  $\text{Si-O-Si}$  bonds. When the number of Si atoms in an oligomer exceeds 3, the molecules begin to adopt ring structures (cyclize), forming a more condensed oligomer than is afforded by a chain-like configuration. Silica monomers and dimers preferentially bond to these cyclic oligomers rather than forming higher order linear oligomers. The condensed oligomers continue to grow through n monomer or dimer additions. In solutions between pH 2 and 7, the oligomer stabilizes when the diameter of the colloids reaches 2 to 3 nm; these colloids may persist for long periods, until condensation reactions cause coalescence and precipitation from the solution.

The observed fourth order rate of dependence with respect to  $[\text{H}_4\text{SiO}_4]$  is consistent with the formation of a critical nucleus with four silica groups during the oligomerization of silica into metastable nanocolloidal silica. The sensitivity of the reaction rate constant,  $k_4$ , to ionic strength and to silica concentration, as a function of pH, suggests that the critical species chemically behaves as a bulk surface. In the brine solution used (employed at  $25^\circ\text{C}$ ), nanocolloids are relatively stable at low pH and at low ionic strength and, thus, such nanocolloids would be expected to occur in natural solutions even as they approach steady state equilibrium with amorphous silica. The form of the log rate (oligomerization) vs. pH curve is roughly the inverse of the form of the log rate (dissolution) pH curve for feldspar dissolution. The determination of the reaction rate is complicated due to the duration of the induction period during which little or no observed oligomerization occurs. The accumulation of precipitated silica is most rapid at the beginning and  $[\text{SiO}_2]_{\text{ppt}}$  increases through time in all experiments until a constant concentration is achieved (steady state). The concentration of silica precipitate becomes constant faster in solutions close to neutral pH. At near neutral pH conditions, nanocolloidal



silica is very unstable and quickly reaches a maximum, then decreases to a concentration at or near 0 millimolal. The oligomerization rate is most rapid at near neutral pH for all ionic strengths. Increasing the initial concentration of silica also increases the oligomerization rate, although in solutions with similar pH and initial silica concentrations, the steady state concentrations of the (molybdate) reactive silica are also very similar. During the induction period it is inferred that critical nuclei form.

A two-step mechanism was proposed for the (silica) polymerization process (Rothbaum and Rohde, 1979): the formation of dimer first (induction period) and then rapid polymer growth of the fourth kinetic order later (Icopini et al., 2005). The length of the induction period increases with temperature and decreases with supersaturation. When a solution initially saturated with silica is suddenly quenched to a lower temperature, silica becomes supersaturated. The lower the final temperature is, the higher the supersaturation. With an increase in salt concentration, the equilibrium concentration of silicic acid decreases. The induction time decreases in proportion to increasing salt concentration.

Silica precipitation involves colloidal growth by nucleation that is an initially first order monomer followed by ultimate deposition of aggregated particles. The reaction falls into two kinetic regions:

Region I is where the initial silicic acid concentration  $C$  exceeds a transitional concentration,  $C_x$ , and polymerization is first order in both the silicic acid concentration,  $C_{SiO^-}$ , and in the surface concentration of ionized hydroxyl groups.

$$\frac{dC}{dt} = -kA_s(C - C_x)C_{SiO^-} \quad (14)$$

where  $A_s$  is the specific surface area. The silica surface charge is influenced by the solution's pH and the salt concentration.

In region II,  $C < C_x$ .

## 2.9 Ionic charge

It was explained (Wahl, 1977) that geothermal brines are aqueous solutions of inorganic salts. These salts ionize to form an ionic solution except for silica, which may form a small percentage of non-ionic material. The salts in the solution are nearly 100% ionized; consequently, the solution is highly ionic and behaves as such. The ionic solution must have equal cationic and anionic charges.

The only reactions that occur in a geothermal brine solution are simple ionic reactions between cations and anions (Wahl, 1977). An exception to this is the reaction of silica to form higher polymers of silica. The solvated cations and anions must be distributed uniformly throughout the solution to maintain a neutral charge distribution.

The ionic equilibrium in geothermal systems is an important control on the chemical nature of hot waters where dissolved salts, which are extensively ionized at ambient temperature, may be incompletely ionized in low-density high-temperature water, and a wide range of ion complexes may form (Ellis and Mahon, 1977). The condition of chemical equilibrium in a geothermal solution requires that the concentrations of all solutes adjust so that the equilibrium constants for all interactions between species are satisfied. For dissociated equilibria, the free energy of dissociation may be separated into an electrostatic contribution arising from the creation or disappearance of ions and the free energy of making or breaking chemical bonds.

According to Chan (1989), previous works suggest that surface charge effects control particle nucleation during the early stages of silica polymerization, but surface rearrangement reactions control continued particle growth as silica precipitation proceeds.

The surface of pure silica in water adsorbs hydroxyl ions (or loses hydrogen ions) and becomes negatively charged in alkaline suspension (Matijevic, 1997). On the other hand, there is no evidence that pure silica surfaces can lose hydroxyl ions and become positively charged in acid solutions. The surface does not adsorb acid as it does base. In this sense, ordinary silica is in an iso-electric condition, that is, the particles do not move when a potential is applied across the solution, at any pH below about 3. The ionic charges on the surface of particles in ordinary silica sols consist of a few strong-acid sites which remain constant in number over a wide pH range, plus additional negative charges at higher pH due to the increasing adsorption of hydroxyl ions or dissociation of silanolic groups.

Due to the very slow formation kinetics of crystalline silica, silica initially precipitates as relatively pure amorphous silica, and then undergoes changes into crystalline silica (Sheikholeslami et al., 2001).

During silica polymerization, the effects of various cations and anions complicate the kinetics and thermodynamics (Sheikholeslami et al., 2001).

Below a pH of 8, silica exists as orthosilicic (monosilicic) acid (as described in 2.8), but above a pH of 8, it ionizes and forms silicate ions (Sheikholeslami et al., 2001); the addition of salts lowers amorphous silica solubility but, in addition, the alkaline environment favours the formation of silicate ions reacting with metal ions and forming insoluble metal silicates.

In tests performed by Sheikholeslami et al. (2001), the preferred operating pH range in absence of cations was either above 9.5 or below 5.5, while in the presence of cations, it was below 5.5.

Nucleation and polymerization give rise to hydrated silica particles  $m\text{SiO}_2 \cdot n\text{H}_2\text{O}$  in the brine (Potapov, 2004). Some of the silanol groups SiOH on the surface of the particles dissociate to release a proton  $\text{H}^+$ , and the particle surface acquires a negative charge. The electrostatic repulsion of negatively charged particles prevents them from coagulating and ensures the stability of the colloidal silica brine. The instability of the colloidal system near the inner surface of a channel leads to silica precipitation from geothermal brine.

## 2.10 Double layer

The double layer is defined (Matijevic, 1997) as the adsorbed anions on the surface and the accompanying cloud of surrounding cations. The charge density can be expressed as the number of electronic charges per unit area. An increase in electrolyte concentration diminishes the thickness of the electric double layer; it also causes an increased adsorption of hydroxyl ions.

## 3. MECHANISM OF NUCLEATION AND GROWTH OF SILICA POLYMERS

Silica particles tend to collide, nucleate and grow according to the pH, temperature, charge and concentration, which are the same factors that determine the polymerization rate. The mechanism is named a gel phase, coagulation and flocculation.

There are two mechanisms for deposition of amorphous silica (Sheikholeslami et al., 2001): growth from monomeric molecules where the monosilicic acid directly reacts with the OH groups on the surface (heterogeneous nucleation), and growth by colloidal particle deposition where it first

polymerizes with other molecules of monosilicic acid (homogenous nucleation), then forms colloidal particles and deposits; silica scaling processes may involve both monomeric and polymeric depositions.

### 3.1 Effect of pH

The basic step in gel formation is the collision of two silica particles with sufficiently low charge on the surface that they come into contact so that siloxane bonds are formed, holding the particles irreversibly together (Matijevic, 1997). The formation of this linkage requires the catalytic action of hydroxyl ions (or the dehydration of the surface of particles at higher pH). The rate of gel formation in the pH range from 3 to 5 increases with pH and is proportional to the hydroxyl ion concentration. Above pH 6, the scarcity of hydroxyl ions is no longer the limiting factor on the rate of gelling. Instead, the rate of aggregation decreases because of fewer collisions between particles due to the increasing charge on the particles, thus decreasing with higher pH. The net result of these two effects is a maximum in the rate of gelling at around pH 5. In the range 8 to 10, sols are generally stable. Once the siloxane bonds have formed between particles, there is a further deposition of silica at the point of contact due to the negative radius of curvature. This occurs rapidly above pH 5, and is slow at pH 1.5. Above pH 3, the addition of salt reduces the overall net repulsion effect and coagulation and gelling are greatly accelerated. The addition of salt to a dilute sol brings about coagulation and precipitation, whereas in a concentrated sol, coagulation is rapid and indistinguishable from gelling.

There is a strong relationship between pH and the precipitation rate of amorphous silica from a supersaturated solution (Grassiani, 1999). pH controls the precipitation rate of amorphous silica more than the degree of supersaturation. So lowering pH may prevent deposition. An example mentioned is the Ormat Mak Ban plant where silica scaling was prevented by lowering the pH from 6.3 to 5.5; some precautions were also taken to avoid corrosion in the event of too efficient scale control or the event of partial lack of brine supply leading to low flow velocity fouling and the subsequent adhesion of suspended silica created at the hot flash stage.

### 3.2 Concentration

The rate of gelling (Matijevic, 1997) appears to be proportional to the total area of silica surface present in a given volume of sol. Since the specific surface area of silica varies inversely with particle diameter, sols, having the same ratio of concentration to particle diameter, gel at about the same rate.

### 3.3 Temperature

Lowering the fluid temperature can decrease the solubility of dissolved silica or metal sulphide species and allow them to precipitate individually or together; boiling decreases both the volume of the residual fluids and their temperature, thereby simultaneously increasing the concentration of the dissolved solids present and decreasing their solubility. The loss of dissolved gases can also affect the pH and solubility (Thomas and Gudmundsson, 1989).

Since aggregation involves a kinetic phenomenon (Matijevic, 1997), the rate of gelling increases with temperature. This is not always so in the case of flocculation, where hydrogen bonding with organic molecules is involved, but in forming gels, there is a marked temperature coefficient of the rate of formation of siloxane bridges between particles.

### 3.4 Gel phase

While a sol is being converted to a gel, the growing aggregates contain the same concentration of silica and water as in the surrounding sol regions; gelling occurs when about half of the silica has entered the gel phase, which can be thought of as spherical particles in suspension which cause a rapid increase in viscosity when the volume fraction reaches about 0.5 (Matijevic, 1997).

### 3.5 Coagulation

Coagulation has been considered the result of van der Waals attraction which draws two particles together at the moment of collision, unless opposed by a hydration barrier layer or by electrostatic repulsion forces between similarly charged particles, or both (Matijevic, 1997).

There are two factors that retard the coagulation of silica (Matijevic, 1997):

1. The hydration of the surface of the particles by a layer of water molecules hydrogen-bonded to the SiOH groups.
2. The negative ionic charge on particles above pH 3.5 and the surrounding cloud of positive counter cations, such as  $\text{Na}^+$ , forming the “double layer”.

For most dilute silica sols around pH 2, where there is little ionic charge on the particle, no coagulation by electrolytes is observed due to the hydration layer.

The silica polymerization and coagulation cations in geothermal brine are (Potapov, 2004):  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ .

### 3.6 Flocculation

Silica sol flocculation occurs when a polymeric or particulate colloid is added, the micelle or particle of which is adsorbed simultaneously on the surfaces of two different silica particles, thus linking them together (Matijevic, 1997). Such adsorption occurs either because the agent is cationic and thus attracted to the negatively charged silica surface, or because it contains electron donor groups such as the oxygen of a polyether, and is held to the silica surface by hydrogen bonding. The latter does not occur at high pH where the silica surface is highly charged, but only at low pH where the surface consists of neutral silanol groups. Thus, organic flocculating agents are (a) cationic surfactants which form micelles, (b) cationic organic polymers, and (c) non-ionic water soluble organic compounds or polymers containing electron donor groups such as ether, hydroxyl, or amide. The type by which silica particles are held together depends on the type of flocculating agent:

1. If the agent is adsorbed on the surface and oriented so that hydrophobic areas are produced, these areas on different particles come together to form a micelle. The particles are held together by powerful surface tension forces around the negative radius of curvature at the zone of contact, the so called hydrophobic bond.
2. The organic polymer or inorganic colloidal particle attaches itself to two different silica particles and acts as a bridge.

Complete flocculation occurs when there is enough adsorbed flocculant to create bridges at an average of three points of contact per particle, so as to form a three dimensional network.

#### 4. SCALING PREVENTION

Particle transport from the flow to the pipe walls occurs by four independent mechanisms (Potapov et al., 2002):

1. Transfer from the flow core to the laminar layer;
2. Transfer through the laminar layer due to turbulent pulsation;
3. Inertial motion of particles; and
4. Brownian diffusion.

The different methods used to prevent scaling are based on the principle of polymerization reduction; if this can be achieved, the silica will not scale. The removal of silica by aging at some temperature for complete silica polymerization, yielding colloidal particles of the desired size, the addition of coagulant (lime), and the separation of the resulting flakes in a settler are not discussed here because the objective of this work is not silica removal, rather the avoidance of silica scaling in order to maximize the use of the geothermal energy.

Silica removal is usually a part of a lime-soda softening process where calcium, magnesium and alkalinity concentrations are reduced (Sheikholeslami et al., 2001).

Results on non-polymeric and polymeric additives to combat silica scaling, where thermal stress causes degradation of polymeric additives (Amjad and Zuhl, 2009), indicate that cationic base copolymers, cationic polymers and surfactants are effective silica polymerization inhibitors but offer poor silica/silicate dispersancy activity, and brine acidification outperforms organic inhibitors. The polymers commonly used as inhibitors for mineral scales and dispersants for suspended matter perform poorly as silica polymerization inhibitors; non-polymer additives were shown to be ineffective silica polymerization additives under high temperature.

##### 4.1 pH modification

A process to inhibit the deposition of ferric silicate scales from high temperature and hypersaline geothermal brines, such as the ones in Salton Sea (Gallup, 1993), was developed. Ferric ions are known as mild steel corrosive agents:



The reduction of ferric ions in geothermal brine by reducing agents is expected to have a mitigating effect on corrosion. The process proposed consists of injecting a reducing agent into the brine to reduce trivalent iron to the divalent state; this also mitigates corrosion of brine handling equipment. Scale deposition is decreased as a result of ferrous silicate being more soluble in these brines than ferric silicate. Scaling can also be controlled by simultaneously blending into the brine a reducing agent and a small amount of acid, sufficient to decrease the pH by about 0.5 units.

An investigation of organic inhibitors (as dispersants) for silica scale control in geothermal brines (Gallup, 2002), with over 25 products, was carried out in the laboratory. Only one single inhibitor showed more than 50% scale deposition reduction compared to no-inhibitor experiments; above the recommended dosage (1 ppm), significant deposition was observed, postulating that overdosing the dispersants leads to flocculation. In contrast, progressive acidification of brine decreased scaling significantly. When the same tests were carried out in a geothermal field, only two inhibitors decreased scale deposition by more than 50%, and most of the products increased scaling.

A continuation of the investigation of silica scale control with organic inhibitors was done (Gallup and Barcelon, 2005) with another series of products consisting of dispersants and phosphine-carboxylic

acid mixtures. Tests were carried out with different products from 7 different vendors in synthetic brine. Brine acidification out-performed the organic inhibitors. A few of these products exacerbated scaling. Acid precursors also appeared to be acceptable alternatives to strong acids as a means to limit corrosion.

#### **4.2 Temperature control**

A study (Gunnarsson and Arnórsson, 2005) explained that polymeric silica has a lesser tendency to precipitate from solution than monomeric silica; that is why silica scales can be avoided during heat extraction by rapid cooling in capillary heat exchangers. It was explained that scale formation from amorphous silica leaving the heat exchanger can be eliminated by aging the water and mixing it with condensed steam.

#### **4.3 Pressure drop control**

Studies on sulphide rich scales show that pressure control can inhibit scaling, keeping a wellhead pressure above 15 bar-g, and amorphous silica scaling can be avoided by keeping the separator pressure above the saturation pressure of amorphous silica (Hardardóttir et al., 2005).

There is a project to extract fluid from the area around CPI and keep the brine pressurized to avoid silica scaling by using high-pressure pumps, and to feed a low-pressure unit of 30 MWe or use it as the primary fluid for a binary plant. The same principle was used in the hot reinjection prototype plant mentioned in Section 1.1.3.

#### **4.4 Electromagnetic control**

Thomas and Gudmundsson (1989) mentioned works where the passage of silica supersaturated brine through a zone of crossed magnetic and electrical fields might substantially increase the rate of silica polymerization and subsequent settling. It was postulated that electrical and magnetic fields might disrupt the electrical double layer surrounding the silica polymers and thereby reduce the strong surface charge effects responsible for the slow rate of silica polymerization.

#### **4.5 Thermodynamics control**

This prevention method refers to heat exchangers designed to minimize scaling. When the solution evaporates due to a pressure drop inside the heat exchanger, the liquid phase turns out to be supersaturated relative to amorphous silica solubility, provoking scaling if the velocity of the fluid is too slow; if the velocity is too fast it may only provoke fouling. Due to mass transfer, the colloid particles from the central part of the solution migrate to the pipe walls and form hard depositions (Kashpura and Potapov, 2001). The heat exchanger design should maximize a rapid interaction with both fluids; this is related to the materials, pipe size and pipe schedule. The design should also minimize the number of pipe bends, avoiding sudden changes of flow direction.

A model to predict the solid deposit growth rate (Potapov et al., 2006) describes the interactions of the particles with temperature, pH and the ionic strength of the brine during deposition in a heat exchanger.

## 5. OPPORTUNITIES

The increase in the efficiency of using a geothermal heat transfer medium is defined by a certain set of factors, among them being the elimination of downtime in geothermal power plants, the production of additional heat and electric power in a binary cycle with a low-boiling heat-transfer medium, and the recovery of a raw material in the form of amorphous silica (Potapov, 2004).

There are several problems in Cerro Prieto attributed to silica scaling, like pressure increase in reinjection wells, efficiency loss in backpressure turbines, heat transfer loss in heat exchangers and an increase in maintenance costs.

Eliminating the scaling problem in Cerro Prieto would help to increase generation without additional drilling, by installing a binary power plant, and by reducing iron silicate scaling in the turbines.

When the scaling problem is finally controlled in Cerro Prieto, and hot brine reinjection is possible, the evaporation pond can finally be removed. This would reduce pollution risks of spillage, eliminate the maintenance costs of channels and pond as well as the silica dragging cost and dragging boat maintenance. A latent danger would also be eliminated by removing the pond, because of the possibility of a rupture of walls during an earthquake and subsequent spillage of highly silica saturated water; this wall rupture could also provoke a huge wave that could damage the infrastructure.

With an increase of the hot brine reinjection rate, increased steam productivity might be expected without additional drilling. Without the silica scaling problem, lower injectivity pressures would be needed to avoid silica precipitation and the pumping system would be simpler and more economical.

Fluids in CP1 are oversaturated with respect to calcite. In this part of the field, either a pumping system would be installed to extract hot brine from the reservoir and send it to the northern low-pressure separation module to feed steam to unit 5, or a binary plant would be installed. Calcium scaling is easier to deal with.

## 6. CONCLUSIONS

An attempt to better understand the silica scaling problem in Cerro Prieto was made by reviewing publications regarding silica polymerization.

It was concluded that scaling is a chemical process consisting of an incubation process followed by polymerization (nucleation of particles and growth) and finally deposition.

Avoiding silica polymerization and scaling might result in an efficiency increase in the system. The main aspects controlling silica polymerization are temperature, pH and concentration; the methods applied to avoid scaling consist of changing the pH or avoiding a sudden temperature drop.

Silica removal has been accomplished in Cerro Prieto by reinjecting the residual brine at ambient temperature, but the goal is to achieve hot reinjection without scaling of the transport pipe and the wells. Reinjection would prevent reservoir pressure drop and reduce boiling and the influx of cooler groundwater.

In the Salton Sea geothermal field, the scaling problem was reduced by reducing the pH by ~0.3 units with hydrochloric acid. The hydrogen ions added during acidification are believed to inhibit iron rich silica scaling.

Polymers are formed by the linking of larger numbers of small molecules. Silica polymerization occurs when its solubility is exceeded. Polymerization is an ionic reaction proportional to the concentration of hydroxyl ions; adsorbed cations serve as bridges between the particles and this bridging effect causes silica particles to adhere and flocculate. There is a thermodynamic tendency to maximize siloxane and to minimize silanol bonds which remain at the surface of particles and serve as nuclei where particle growth occurs. Some of the silanol groups on the surface of the particles dissociate to release a proton  $H^+$ ; the particle surface acquires a negative charge, that prevents coagulation. These surface charge effects control particle nucleation in the early stages of polymerization but surface rearrangement reactions control continued particle growth as silica precipitation proceeds.

The double layer is defined as the adsorbed anions on the surface and the accompanying cloud of surrounding cations. An increase in concentration causes an increased adsorption of hydroxyl ions.

The driving force for nucleation and polymerization is supersaturation which is accompanied by the formation of siloxane bonds and partial dehydration.

The amorphous silica precipitation mechanism is controlled by the surface defect/surface nucleation process and not by aqueous diffusion or elementary reactions at the solid-solution interface. The basic step is the collision of two silica particles with sufficiently low charge on the surface so that when they come into contact siloxane bonds are formed, holding the particle together. Once the siloxane bonds are formed, further deposition of silica takes place at the point of contact due to the negative radius of curvature.

The precipitation rate of amorphous silica is controlled by the pH, so lowering the pH prevents deposition.

It may be expected in Cerro Prieto brine that silica would form polymers with internal condensation and cross-linking, where hydroxyl groups attached to silicon only on the outside due to the alkaline nature of the fluid. Hydroxyl ions catalyse dissolution and deposition of silica; the smaller particles dissolve and the larger ones grow. Silica deposition is kinetically controlled and can be delayed after its saturation limit has been exceeded.

In Cerro Prieto the pipe scaling problem has been reduced by maintaining a pipe size big enough to reduce pressure drop and low enough to avoid small velocities that may produce silica precipitation or fouling. In the turbines the iron silicate scaling has been reduced by periodical steam and turbine wash.

It is expected that once the silica scaling problem is controlled, hot brine reinjection can be achieved and the pressure drop effect in the reservoir can be minimized, as well as the influx of cooler groundwater. An increase in efficiency and productivity can also be achieved by avoiding adverse silica scale effects.

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