# Chapter 9

# CORROSION AND SCALING

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## 9.1. INTRODUCTION

The chemical nature of most geothermal fluids poses some severe technical constraints to the utilisation of geothermal energy, and especially of the high-enthalpy part. Geothermal fluids contain various quantities of soluble species (up to 300 g/kg of fluid) and dissolved gases, which under the thermodynamic changes occurring during their utilisation may result in scaling (or generally speaking fouling), corrosion of the metallic surfaces in contact with the fluids and even environmental problems (emission of harmful gases, liquid disposal etc.). Another intrinsic characteristic of geothermal energy is that the geothermal fluids vary greatly from site to site and for this reason measures taken to cope with these problems in one site may not be applicable to another site.

The control and prevention of the corrosion and scaling problems has evolved over the past 50 years from the empirical approach and an 'a posteriori' treatment (chemical and/or mechanical removal of scales, replacement of heavily scaled or corroded sections) to systematic research towards understanding the complicated phenomena leading to these problems and taking measures to mitigate them. In this direction the knowledge acquired from other sectors (e.g. oil production, chemical industry, power generation) in dealing with similar problems contributed significantly to our understanding.

The objective of this chapter is to offer a general description of the problems of scaling and corrosion in geothermal plants and to discuss the most common measures to mitigate these problems.

## 9.2. SCALING IN GEOTHERMAL PLANTS

### 9.2.1. Definitions

Fouling is defined as the accumulation of undesirable materials in the surfaces that come in contact with certain fluid. Fouling can be found in almost every industrial, domestic or physiological activity which involves fluid flow, with or without heat transfer via the surface. The problems related to fouling are not recent. The Ancient Greeks and the Romans, more than twenty centuries ago, had encountered problems of calcium carbonate deposits in aqueducts (Cowan and Weintritt, 1976).

*Precipitation or crystallization fouling* occurs in a geothermal system whenever the ionic product of a sparingly soluble salt exceeds its equilibrium solubility product.

The terms scaling or scale formation are commonly used when the precipitate formed is a hard deposit. Scaling often refers to the formation of deposits of inverse-solubility salts (e.g. $CaCO_3$, $CaSO_4$, $Ca_3(PO_4)_2$), although this term in industry denotes the hard and adherent deposits that form in equipment from the inorganic constituents of water.

Particulate fouling and biofouling, two other types of fouling as categorised by Epstein (1978), can also occur in geothermal plants and in geothermal heat pumps systems, usually with no significant consequences. Particulate deposits have been observed in low enthalpy fluids rich in fer-rous ions (Andritsos et al, 1994). Severe problems from particulate deposits can occasionally occur in the reinjection formation with pore blocking. Biofouling is a rare occurrence in the geothermal systems due to high fluid temperatures and the problems are limited in the cooling water systems and in open-loop geothermal heat pump systems.

The formation of scale on equipment surfaces exposed to geothermal fluids can have serious economic consequences, arising out of energy losses, increased capital cost from equipment oversizing, increased pumping costs, increased cost of cleaning and maintenance, loss of production, or even abandoning a production or reinjection well due to clogging. With intensified efforts to use geothermal resources for energy production and for other industrial applications, there is an increased interest in understanding the scaling process. An improved understanding may lead to measures for mitigating this problem.

The great complexity of the scale formation process results from the large number of species found in a geothermal fluid and from the plethora of possible physical mechanisms involved. The latter may include mass, momentum and heat transfer, as well as chemical reactions at the equipment surfaces. Furthermore, the diversity of fluid composition from site to site and the variation of processes along the flow path make difficult the generalization of both the mechanisms responsible for the scale formation and the preventive measures.

Scale formation may occur almost everywhere in a geothermal plant. It may occur in the geothermal formation, geothermal wells, surface facilities, reinjection line and well, cooling water system and turbine blades.This presentation will not deal with cooling water fouling in geothermal plants, since this problem is treated properly in numerous publications (Kemmer 1988, Betz-Dearborn 1991).

### 9.2.3. Scale Composition in Geothermal Systems

The composition of the scale in geothermal plants is commonly very complex and depends on many parameters, such as the temperature and pressure of the fluid, the history of water-rock interactions and the operating conditions. Low and moderate temperature brines (T<150°C) yield, as a rule, scale consisting of calcium carbonate (Owen and Michels, 1984; Corsi, 1986).

There are a few exceptions to this rule, such as the geothermal wells in the Paris Basin, where relatively large concentrations of iron and dissolved sulphide result in iron sulphide scale deposits (Criaud and Fouillac, 1989). High enthalpy and low salinity fluids usually form silica scale (e.g. certain wells in Iceland). On the other hand, high temperature liquids with high TDS content yield both siliceous and sulphide scale, with lead sulphide being one of the major constituents. Table 9.1 gives some examples of the various scale types occurring in low and high-enthalpy geothermal systems. Pictures of scaled geothermal pipes are included in Figure 9.1.

### 9.2.4 Basic concepts of scale formation

For an ionic substance $M_nA_m$, that crystallises according to the reaction

$$nM^{a+} + mA^{b-} \Leftrightarrow M_nA_m \text{ (solid)}$$

the thermodynamic driving force for the crystallisation either in the bulk or at the pipe substrate is defined as the change of the Gibbs free energy of transfer from the supersaturated state to equilibrium:

$$\Delta G = RT \ln \left[ \frac{(M^{a+})^n (A^{b-})^m}{K_{sp}} \right]^{1/(n+m)} = RT \ln \left[ \frac{IAP}{K_{sp}} \right]^{1/(n+m)} \qquad (2)$$

Table 9.1. Scale composition in geothermal systems.

| **Earth Energy (Geothermal Heat Pumps)** | |
|---|---|
| *Component* | *Examples* |
| *Calcium carbonate* | • Various sites |
| *Iron oxides* | • Various sites |

| **Low and medium-enthalpy fluids** | |
|---|---|
| *Component* | *Examples* |
| *Calcium carbonate* | • N. Kessani, Sousaki, Nigrita (Greece), Kizildere (Turkey) |
| *Iron oxides* | • Nigrita (Greece) |
| *Iron sulphide salts* [in association with corrosion] | • Dogger Basin (France) |

| **High- enthalpy fluids** | |
|---|---|
| *Component* | *Examples* |
| *Calcium carbonate* | • Miravalles (Costarika), Latera (Italy), Cerro Prieto (Mexico), East Mesa, Nevada (USA) |
| *Silica (and metal-silicates)* [usually associated with small or medium TDS] | • Svartsengi (Iceland), Matsu Kawa (Japan) |
| *Heavy metal sulphide salts* (with silica and metal-silicates) [associated with high TDS] | • Salton Sea (USA), Milos (Greece), Asal Wells (Djibouti) |
| *Oxides* (and sulphide salts) | • Reykjanes (Iceland) |

TDS: Total Dissolved Solids (mg/kg)

Figure 9.1. Pictures of scaled geothermal pipes. Left, $CaCO_3$ scales in a pipe carrying low-enthalpy geothermal water at Nigrita, Greece. Right, mixed silica and sulphide scales in the reinjection pipe of Milos geothermal plant.

In the above equation, R is the gas constant, T the fluid temperature, $K_{sp}$ the thermodynamic solubility product of the phase forming compound and (IAP) the ion activity product. Quantities in parentheses denote activities of the corresponding ions. The quantity is defined as the **supersaturation ratio** of the crystalline precipitate. For scale formation to occur, S must exceed unity.

$$S = \left[\frac{(M^{\alpha+})^n (A^{\hat{a}-})^m}{K_{sp}}\right]^{1/(n+m)} = \left[\frac{IAP}{K_{sp}}\right]^{1/(n+m)} \quad (3)$$

Often, in the literature, S is written without the exponent. Today, the solution speciation and the supersaturation ratios of the various salts in geothermal waters are readily computed by various computer codes taking into account all possible ion-pairs and the most recent values for the solubility products and the dissociation constants.

Of primary importance is the development of supersaturation which is the driving force for nucleation and crystal growth. Provided that there is sufficient contact time with a foreign substrate, scale formation may take place. Supersaturation can be achieved as a result of the change of the operating conditions, most notably of temperature and of pH.

In Figure 9.2 a typical solubility diagram for a *sparingly soluble salt of inverse solubility* (such as $CaCO_3$, $CaSO_4$) is shown. The solid line corresponds to equilibrium. At a point A the solute is in equilibrium with the corresponding solid salt. Any deviation from this equilibrium position may be effected either isothermally (line AB), at constant solute concentration, increasing the solution temperature (AC), or by varying both concentration and temperature (AD). A solution departing from equilibrium is bound to return to this state by the precipitation of the excess solute. For most of the scale forming sparingly soluble salts, supersaturated solutions may be stable for practically infinite time periods. These solutions are called *metastable*. There is, however, a threshold in the extent of deviation from equilibrium marked by the dashed line in Figure 2, which if reached, first wall crystallisation (scaling) and subsequently spontaneous precipitation may occur with or without an induction period preceding precipitation. This range of supersaturation defines the *labile* region and the dashed line is known as the super solubility curve. It should be noted that the super solubility curve is not well defined and depends on several factors such as presence of foreign suspended particles, wall material and roughness, temperature, pH etc. The formation and subsequent deposition of solids occurs only when the solution conditions correspond to the metastable or the labile region. Below the solubility curve scaling cannot take place.

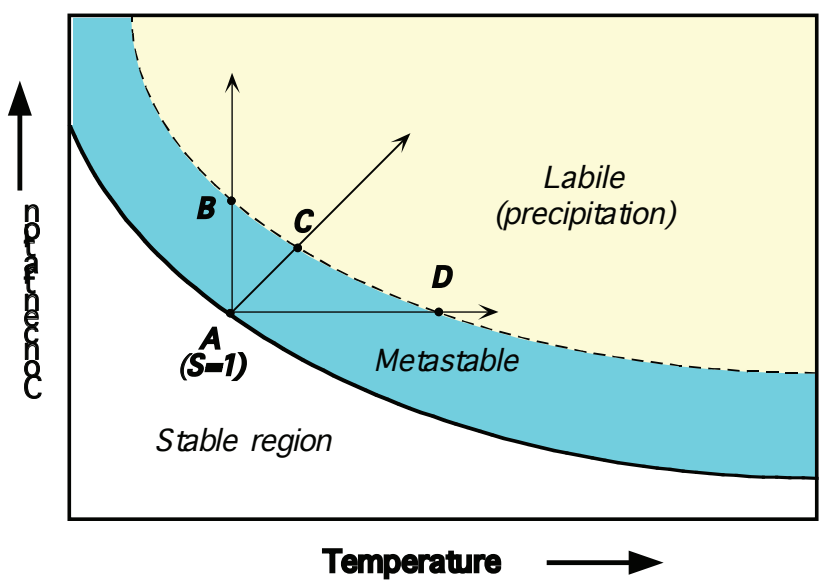


Figure 9.2. Solubility-supersaturation diagram of a sparingly soluble salt with inverse solubility.

### 9.2.5. Common Types of Geothermal Scale

The following is a short discussion of the common types of geothermal scales. Although they will be dealt with individually, deposits in geothermal systems are rarely homogenous and usually more than one phase is identified.

*a) Calcium Carbonate*

Calcium carbonate forms a dense, extremely adherent deposit. It is by far the most common scale problem in low and medium temperature geothermal systems. Calcium carbonate deposits can be also encountered in heat pump systems (Rafferty, 2000). The mechanism of $CaCO_3$ scale formation can be described as follows: almost all geothermal fluids contain significant quantities of dissolved $CO_2$, in the form of $CO_2$(aq) and $HCO_3^-$. The flashing of the vapour phase and the $CO_2$ release cause a pH increase. As a result supersaturation conditions are established and $CaCO_3$ is deposited:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \text{ (solid)} \quad (4)$$

Apart from the assessment of the $CaCO_3$ scaling tendency using the supersaturation ratio, this tendency can be predicted qualitatively by a plethora of indices derived theoretically or empirically over the past 70 years. The most common indices are the Langelier Index and the Ryznar Index.

Calcium carbonate can exist in three different polymorphs, namely calcite, aragonite and vaterite, in order of increasing solubility. All three polymorphs have been identified in scales, although vaterite is rather rare. Thermodynamics predicts that calcite, the least soluble polymorph, should be the phase favoured in the precipitation process. Aragonite is also encountered in geothermal systems, forming scales sometimes as tenacious as those of calcite. The water temperature and chemistry (e.g. pH and ionic strength) have been shown to play a determining role for the nature of the precipitating calcium carbonate phases. It is also well known that the presence of magnesium ions, in solutions supersaturated with respect to $CaCO_3$, favours the precipitation of aragonite and appears to hinder the formation of vaterite.

*b) Heavy Metal Sulphides*

Regarding the mechanism of sulphide scale formation, two opposing phenomena take place as the brine flashes (Owen and Michels, 1984). For mildly acidic fluids, such as that of Milos, Greece, most of the sulphide species enter the vapour phase in the form of $H_2S$, causing a desirable decrease of those species in the residual brine. However, the pH rise due to the simultaneous release of carbon dioxide favours the precipitation of heavy metals as sulphides (Michels & Owen 1984, Andritsos & Karabelas 1991). The heavy metals at the high temperatures of the brines are mainly transported as chloride complexes. Additionally, the precipitation of metal sulphides is promoted by two other factors, i.e. the temperature decrease, since the solubility of most sulphides significantly increases with temperature, and the "enrichment" of the residual brine in heavy metals because of steam separation.

As an example, in the case of Milos Plant the solubility of galena in the residual brine is estimated to decrease approximately 50 times, by using Helgeson's (1969) data, for a pH decline of 1 unit. These estimates are based on the assumptions that after flashing 50% of the fluid is separated as steam and that the pH of the residual brine increases by one unit, whereas the temperature declines by 20°C. The dependence of the solubility of several heavy metal sulphides upon temperature and pH is illustrated in Figure 3. Sulphide scaling results in bands of hard and tenacious deposits.

Regarding the iron sulphide deposits encountered in the Paris Basin, the mechanism of scale formation of the various polymorphs can be described in brief as follows (Fouillac & Criaud, 1989):

1. Corrosion of the well casing results in the presence of significant quantities of iron in the brines according to the reaction:

$$Fe^{o} \rightarrow Fe^{2+} + 2e^- \quad (5)$$

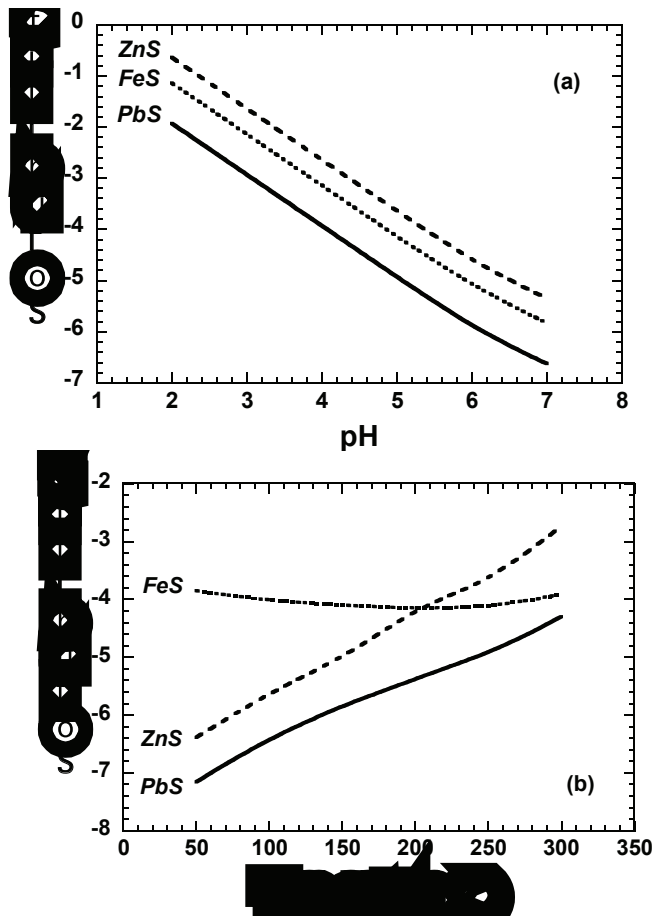


Figure 9.3. Solubility of heavy metal sulphides at 2 N NaCl solutions as a function(a) of pH at a constant temperature of 250ºC and (b) of temperature at pH=7.

A part of the dissolved iron in the fluids comes from the geothermal formation, its concentration being usually less than 1 mg/L. The most important source of dissolved iron is the corrosion of mild steel casing.

2. Bacterial reduction of sulphate ions ($SO_4^{2-}$) to sulphide ones ($HS^-$, $S^{2-}$).
3. Reaction of iron and sulphide ions and the precipitation of various iron sulphide phases (FeS, $Fe_2S$ etc.)

$$(1+x)Fe^{2+} + HS^- \rightarrow Fe_{(1+x)}S + H^+ \quad (6)$$

Obviously, a measure to mitigate the problem is the prevention and control of corrosion of the pipes.

*c) Silica and metal-silicates*

Amorphous silica ($SiO_2$) is deposited from virtually all high temperature geothermal fluids and sometimes from some medium temperature fluids. The mechanism of silica deposition is neither simple nor well understood. In contrast to $CaCO_3$ and sulphide salts, silica deposition is controlled by the polymerization kinetics of silicic acid, $Si(OH)_4$ (Ellis & Mahon, 1977). As a result of the slow polymerization kinetics, silica deposits are formed several minutes or even hours after the establishment of supersaturation conditions. A pH increase favours the polymerization at pH <8.6, although the silica solubility remains unaffected. The polymerization rate at pH<9 depends on pH (or $[OH^-]$), according to the relation (Buhlmann et al., 1980):

$$-\frac{d[Si(OH)_4]}{dt} = k\,[Si(OH)_4] - [Si(OH)_4]_e^2\,[OH^-]^{-0.7} \qquad (7)$$

In the above relation k is the reaction constant, which depends upon the surface area of the deposits and e denotes the silica concentration at equilibrium with amorphous $SiO_2$. In practice for pH less than 5 this reaction is very slow and the silica deposition is practically zero.

In certain geothermal fields, such as Salton Sea in California and Kyushu in Japan, iron and aluminium are incorporated in the amorphous silica deposits by forming bonds of the type Fe-O-Si and Al-O-Si (Gallup, 1993), to form the so-called metal-silicates. It is believed that the rate of deposition of silica is enhanced in the presence of aluminium an iron ($Fe^{2+}$ and $Fe^{3+}$) ions. Although the aluminium concentration in geothermal fluids rarely exceeds 5 mg/kg, its contribution to scale can reach 10% w/w (as $Al_2O_3$).

Another characteristic of the silica deposits is that they are present in every part of the geothermal installation and they are not confined to a relatively short part immediately after the flashing point. A significant problem is encountered in brine reinjection systems, where the precipitated silica colloids can block the pores of the reinjection formation.

### 9.2.6. Scale Control and Prevention

There are numerous methods in use to control scale formation in geothermal systems. Some of the most common measures are the proper design of the geothermal plant and selection of operating conditions, pH adjustment, use of chemical additives and the removal of deposits by chemical or mechanical means. Some typical measures, to be taken in the selection of design and operating conditions, are outlined below:

- Flashing in the wellbore should be avoided by maintaining higher pressure in the well. Reaming of the well is the most effective way to remove the deposits in the casing, but it is rather difficult to remove scale from the slotted liner. Surface equipment plugged by scale can be cleaned easier and more economically than the wellbore. The use of submersible pumps to keep the pressure of the whole system at a pressure higher that needed for flashing is recommended for the low enthalpy situations.
- Careful adjustment of primary flashing pressure in high-enthalpy plants, at a sufficiently high level, can drastically reduce scale formation by keeping solids saturation relatively low. This pressure adjustment is usually effective on silica deposition, but apparently cannot influence sulphide scaling.
- Large pipe diameters may offer some advantages in reducing the impact of carbonate and sulphide scaling, especially in areas where deposition is expected (after flashing point). This suggestion is a direct consequence of the fact that for these scaling systems the deposition mechanism appears to be controlled by the rate of transport of scale-forming ions towards the pipe walls.
- The prevention of shut-downs and of operating condition changes may be of help in certain cases, by avoiding the formation of bands of deposits of reduced adhesion strength. Such deposits can be sometimes shattered and dislodged from the pipe walls, transferred by the flow, and finally accumulated and cemented at certain places. Such problems have been observed for both low and high enthalpy geothermal fluids in Greece. In these cases, special ports at the lower parts of the geothermal system must be installed to collect these deposit fragments.

Carbonate deposits can be prevented by the use of scale inhibitors, as will be discussed below, but the use of inhibitors in preventing sulphide and silica scaling is met by limited success. It seems that these scale types can be prevented (at least partially) by pH decrease with the addition of a mineral acid. The least desirable method is the removal of deposits. However, under some circumstances this method is the only applicable technique. $CaCO_3$ can be dissolved

easily by almost all strong acids; however, corrosion inhibitors have to be used simultaneously. This technique can be used to clean some specific pieces of equipment (e.g. heat exchanger, flashing valve etc.). Chelants cannot be used in the removal of carbonate deposits, because of the slow rate of removal and the large quantities needed. Non-carbonate deposits are difficult to remove by chemical methods and their removal is carried out by mechanical means (e.g. well reaming, mechanical scraping, hydroblasting, etc.).

Finally, it should be stressed that when dealing with a scaling or corrosion problem in a geothermal system one has to take into consideration the following:

(1) There is no specific 'recipe' to deal with all the variations of scale formation.

(2) An effective scale control measure in a geothermal installation may become ineffective in case of change of the operating conditions or when applied to another geothermal system.

### 9.2.7. Control of $CaCO_3$ scale formation

As discussed previously, there are several methods to eliminate or suppress the formation of scale in geothermal and other scale-prone systems (chemical/mechanical cleaning, acidification, chemical complexation, water softening, electro-magnetic gadgets, chemical additives etc); however, most of these methods are not practical, because of the vast volumes of geothermal waters involved. Apart from the cleaning method, which can be used only when a specific piece of equipment (e.g. a heat exchanger) is plagued by scaling, the two most important methods are based on the following concepts:

- Interfering with the crystal nucleation and growth processes (crystal growth inhibitors).
- Reducing the availability of carbonate ion by acidification (injection of strong acid) or by keeping the geothermal brine under pressure by using downhole pumps (Owen & Michels, 1984).

*Crystal Growth Inhibition*

One of the most common techniques to control carbonate scaling involves the *use of chemical additives* (*crystal growth or scale inhibitors, antiscalants*). These substances are usually moderately large molecules that are readily adsorbed on the growth-active sites of the crystal surfaces, thus retarding nucleation and crystal growth and distorting the crystal structure of the scale. The state of the art on the scale inhibition can be found in some recent reviews (e.g. Amjad, 1996). Crystal growth inhibition is considered the most efficient method of control-ling carbonate scale formation in geothermal installations (Vetter & Cambell, 1979; Benoit 1990).

Scale inhibition efficiency depends on the ability of the inhibitor to interfere with the scale formation stages, either in the stage of nucleation or in the stage of crystal growth. The various inhibitors are considered to act according to one (and usually more than one) of the following main mechanisms of interference with crystal growth:

(i) *Threshold effect*: the inhibitor acts by retarding salt precipitation.

(ii) *Crystal distortion effect*: the inhibitor interferes with crystal growth by producing an irregular structure (usually rounded surfaces) with poor scaling potential.

(iii) *Dispersion:* inducing a charge on crystal surface results in the repulsion between neighbouring crystals.

(iv) *Sequestration or chelation*: the binding with certain cations (Fe, Mg, etc) to form soluble complexes.

Theoretical calculations to estimate the antiscalant dose for a specific application are not available and the selection of the appropriate inhibitor and the optimum dose relies on laboratory and field experiments. The most common way to check the effectiveness of an inhibitor is to monitor the calcium concentration in a specific site of the plant. The inhibitor dose in geothermal water depends on the water quality and temperature. The concentration of the antiscalants ranges between 2 and 20 mg/L, but as high as 50 mg/L concentrations have been reported. Blends of different antiscalants are usually used, which sometimes perform bet-

ter than their individual components.

There are several types of inhibitors, the most important in geothermal applications are the phosphorous-containing compounds (inorganic polyphosphates and organophosphorous compounds, most notably phosphonates) and the polycarboxylates (products of polyacrylic, maleic and polymethacrylic acid, of polymaleic anhydrite etc.). A large number of polymers are used as scale inhibitors and as dispersants. Most of the polymers have a molecular weight below 50,000. A typical phosphonate has the following structure:

$$-RCH_2-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O-}{|}}{P}}-O-$$

This structure of phosphonates with C-P-O bonding is more stable to hydrolysis than the polyphosphates. The crystal distortion effect of the inhibitors can be seen in the Scanning Electron Micrographs presented in Figure 9.4.

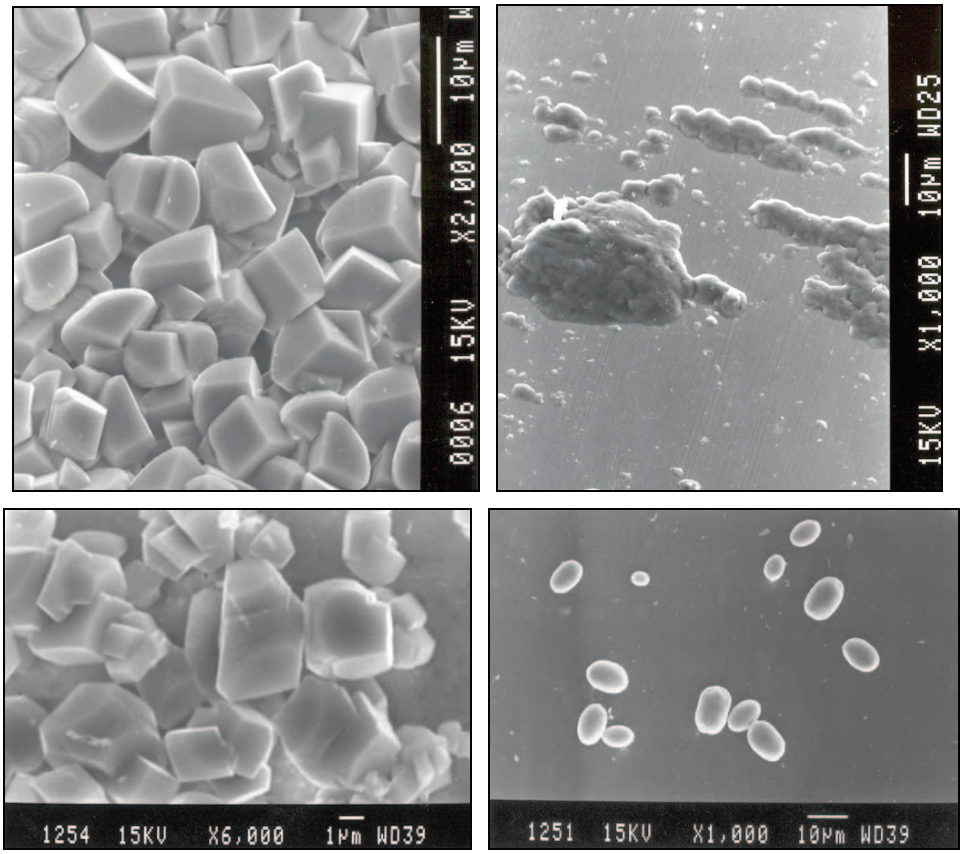


Figure 9.4. SEM micrographs of calcite scales in the laboratory in the absence (a) and in the presence (b) of 5 mg/L of a phosphonate inhibitor. Evident is the reduced scale mass and the crystal distortion in the presence of the inhibitor. In both cases XRD analysis has shown that the deposits are composed of calcite. Micrographs (c) and (d) represent $CaCO_3$ bulk precipitates in the absence and in the presence of the inhibitor, respectively (Andritsos et al, 1996).

The most suitable method of the use of additives in geothermal systems is the continuous downhole injection at a point upstream of the vapour flashing. Rarely the injection of the inhibitors is done batchwise. A typical inhibitor injection system is presented in Figure 5 (Pieri et al. 1989). A flexible tube (o.d. 5-10 mm) is placed in parallel to the well casing or inside the well. In low enthalpy systems plastic tubes may be suit-

able, but for the highly corrosive environments of the high-temperature fluids corrosion resistant materials are needed (e.g. Incolloy, Hastelloy). Downhole inhibitor injection has the advantage of allowing the parallel use of corrosion inhibitors, but it is also associated with the following operating problems:

(1) Ineffective scale control due to low inhibitor concentration.

(2) Probable formation of pseudo-scales (e.g. calcium phosphates). In this case a reduction of the inhibitor concentration or change of the inhibitor is required.

(3) Corrosion of the injection tube due to the corrosive nature of both the geothermal fluid and the inhibitor itself. The phosphonates are strongly corrosive at high concentrations. Pieri *et al.* (1989) suggest the use of alloy Hastelloy C-4 with inner Teflon coating.

(4) Blocking by scales of the tube exit. A continuous additive injection is required in dealing with this problem.

(5) Most inhibitors are unstable (or ineffective) at high temperature (>200°C).

Finally, it is pointed out that the use of inhibitors does reduce the thermodynamic tendency of the fluid to precipitate due to its supersaturation. The fluid remains supersaturated and it is possible that at long residence times the effectiveness of the inhibitor is reduced.

### 9.2.8. Control of Sulphide and Silica Scale

Total prevention of sulphide scale for-mation seems almost impossible at present. However, certain convenient measures may suppress the amount of scale forming in geothermal plants. The main approaches in this direction are the chemical modifica-tion of the brine (e.g. pH reduction), careful design of the plant, the selection of appropriate operating conditions, brine hand-ling and use of additives (mainly crystal growth inhibitors). In a recent study on the assessment of silica scale inhibitors, Gallup (2002) suggests that organic inhibitors will likely continue to have limited use in geo-thermal systems. The least preferable ap-proach to control scale formation is removal of scale by chemical or mechanical means during periodic plant interruptions, unless this cleaning is carried out to a limited degree during regular plant maintenance.

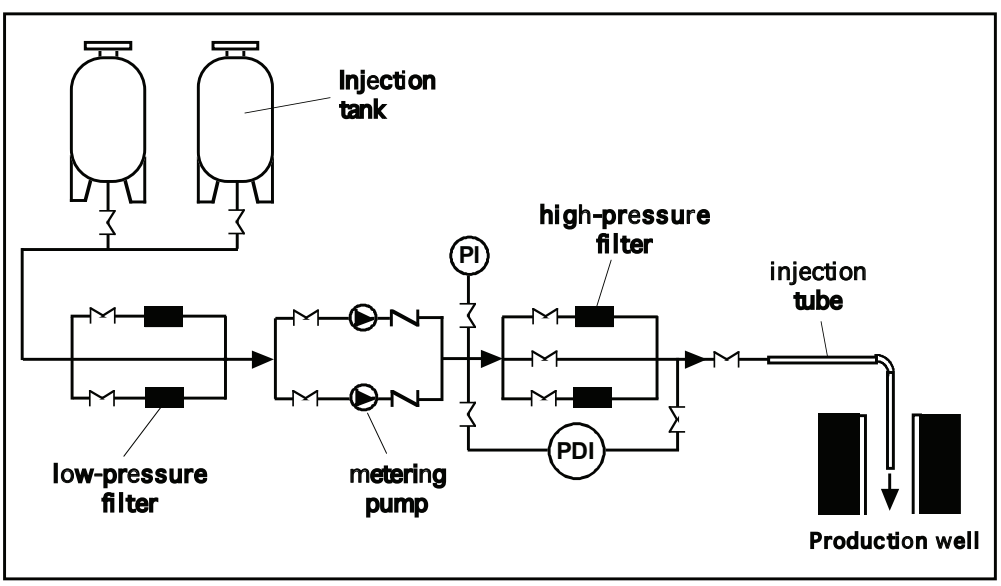


Figure 9.5. Simplified schematic diagram of the inhibitor injection system (Pieri et al, 1989)

*pH Reduction*

The method of sulphide scale control by reducing the pH of geothermal brine is based on the well known fact that the solubility of sulphides increases markedly in acidic solutions. In the range of pH values which are typical of high salinity and high enthalpy brines (pH<6), a ten-fold increaseof the sulphide solubility is obtained by reducing the pH by one unit. Even a small reduction of pH may sometimes reduce drastically the amount of deposits. A reduction of pH will also have a beneficial effect on the formation of silica and metal-silicate deposits. However, two negative factors must be also considered; i.e. the possible corrosion of pipes at low pH values and the cost of acid.

The method of brine acidification has been successfully applied in several cases. Gallup (1996) reports that inhibition of iron-silicate scale is achieved by lowering the pH by only 0.1 to 0.3 units. Also, Harrar (1981) notices that the pH reduction in laboratory experiments inhibits the deposition of both silica and sulphides. However, for complete scale prevention the brine pH should be reduced to about 3, which tends to increase significantly the corrosion rate of steel.

***Brine handling***

The process aims at precipitating and subsequenty settling of the soluble species in specially designed equipment, so that no scaling can occur in the downstream installlation. It is often used when there is the risk of clogging the reinjection well and aquifer.

## 9.3. CORROSION IN GEOTHERMAL PLANTS

### 9.3.1. Definitions

Corrosion of equipment employed for handling geothermal fluids as well as in the production and injection well casings is a serious problem limiting the exploitation of geothermal energy. In this section the corrosion types most commonly encountered in geothermal systems are presented and the main approaches for mitigating this problem are outlined.

As mentioned earlier, geothermal fluids contain chemical species at sufficiently high concentrations which render them highly corrosive. These components include Cl-, $H_2S/HS^-$, $SO_4^{2-}$ and $HCO_3$-. In addition $O_2$, H+ and F- ions contribute to corrosion of metals used in geothermal installations (Ellis 1981, Corsi 1986). The corrosivity of the various geothermal fluids varies widely, depending mainly on their chemical composition.

Additional factors contributing to the corrosion of metals in differing forms include the condition of the fluids, temperature, flow rate, etc. Knowledge of the corrosion processes involved in handling geothermal fluids is of paramount importance in the design of equipment and of the approach to prevent or reduce corrosion phenomena.

Corrosion is the natural process of deterioration of metals and alloys in a corrosive environment. This is a very broad definition, but corrosion occurs in a wide variety of forms, both in pure metals and in alloys. Although some of the forms of corrosion are unique they are interrelated. The two most frequently occurring forms of corrosion are general corrosion and pitting.

### 9.3.2. Types of Corrosion

A number of different types of corrosion have been observed in geothermal systems. The most significant of these types are presented briefly below:

**General or Uniform Corrosion.** General corrosion is the most common type of corrosion. It is defined as the uniform loss of metal from the entire exposed surface of the metal. For most geothermal applications and in the absence of atmospheric oxygen, the general corrosion rate is usually low. However, the simultaneous presence of $O_2$ and $H_2S$ in geothermal fluids can lead to substantially increased corrosion rates. The general corrosion in geothermal systems is responsible for the greatest loss of material, without however leading to severe material failure that characterizes other coorosion types.

**Pitting Corrosion.** Pitting is a type of localized corrosion in which a small portion of the exposed surface experiences very

high corrosion rates resulting in small holes in the metal surface. This type of corrosion usually occurs when general corrosion rates are low. Pitting is especially dangerous because the metal loss rates can be very high. The result is unexpected failures in pipes and tubes. The omnipresent chlorides in geothermal systems is the primary agent for this corrosion type in steels, while for the copper alloys major responsibility lies on the ammonium ions. Pitting corrosion comprises a severe problem in heat exchangers due to thin walls of the pipes or plates. Most importantly, a single hole in a plate heat exchanger can make it inoperable.

**Crevice Corrosion.** Crevice corrosion is another form of localized corrosion. It occurs in crevices on metal structures. Corrosion materials build up in the space of the crevice and create a highly localized and very corrosive environment. Certain anions, such as chlorides, promote the hydrolysis reactions that cause the problem.

**Underdeposit Corrosion.** This is a special type of crevice corrosion where the crevice or space is caused by a deposit on the metal surface. Scale, corrosion products or a variety of other debris can cause deposits under which accelerated corrosion occurs. After deposits are formed, it is difficult to stop underdeposit corrosion, because the deposits make it difficult to get corrosion inhibitors to the metal surface suffering the high corrosion rates. Another form of underdeposit corrosion common in open recirculating cooling systems is caused by the attachment of biomasses to metal surfaces. The biomass produces by- products that are corrosive to most metals and are held next to the metal surface by the biomass.

**Galvanic Corrosion.** When dissimilar metals are connected in an electrolytic solution under the proper conditions, one metal will experience accelerated corrosion. The alloy highest in the galvanic series will corrode faster. The relative areas of the two alloys are important. If the area of the more active alloy is small compared to the area of the noble metal, then the severity of the galvanic attack will be greater. An example of this type of corrosion is shown in Figure 4:

**Impingement.** Impingement is an accelerated form of corrosion that occurs when a metal surface, covered by a protective film, is damaged by mechanical or hydraulic wear or abrasion. Mechanical abrasion will remove protective films, but the effect of high fluid velocity, intense turbulence and cavitation can accelerate this process. These effects are most often observed at inlets to heat exchanger tubes, at piping elbows, in piping downstream of pumps, and on pump impellers. Copper and copper alloys are especially sensitive to impingement.

Figure 9.6. Underdeposit corrosion in carbon steel pipes from the villeneuve La Garenne

### 9.3.3. Operational Factors Affecting Corrosion Rates

**Temperature.** As a general rule, increaseing temperature increases corrosion rates. This is due to a combination of factors- first, the common effect of temperature on the reaction kinetics themselves and the higher diffusion rate of many corrosive by-products at increased temperatures. This latter action delivers these by-products to the surface more efficiently.

Occasionally, the corrosion rates in a system will decrease with increasing temperature. This can occur because of certain solubility considerations. Many gases have lower solubility in open systems at higher temperatures. As temperatures increase, the resulting decrease in solubility of the gas causes corrosion rates to go down.

**pH.** Corrosion rates almost always increase with decreasing pH (increasing acidity). This is a direct result of increasing the concentration of an aggressive ion (H+) and increasing the solubility of most potentially corrosive products.

**Oxygen Concentration.** Oxygen's role in corrosion is as an aggressive gas or oxidizing agent. As its concentration increasees, corrosion rates increase until the rates of diffusion to the surfaces reach a maximum. The same principles apply to most other oxidizing agents, such as $Cl_2$, H+, $Br_2$.

**Fluid Velocity.** The dependence of corrosion rate on fluid velocity is complex. In general, the higher the velocity, the higher the corrosion rate. At very low velocities, even zero, there are diffusion effects that can cause corrosion. As fluid velocities increase from stagnant to moderate values, the corrosion rates increase. Then, as the limit of diffusion at a particular temperature is reached, further increases in velocity have little effect on the corrosion rate. At some point, however, the velocity reaches such high values that the surface film of the metal begins to be damaged. At these velocities, the corrosion rates resume increasing with the higher velocities.

**Suspended Solids.** An increase in suspended solids levels will accelerate corrosion rates. These solids include any inorganic or organic contaminants present in the water. Examples of these contaminants include clay, sand, silt or biomass.

Ellis (1981) devised an empirical system for the classification of the geothermal fluids according to their corrosivity taking into consideration the most important corrosive constituents of the fluids. Of primary importance in the system of Ellis is the total concentration of the corrosive ions. (Total Key Species, TKS). This parameter is analogous to the expression of total dissolved solids (TDS) used for the salt content of a fluid and they are the sum of the chloride, sulfate, carbonate, bicarbonate and of the ammonium ions. For the majority of the geothermal fluids TKS is made of chloride, bicarbonate and carbonate ions. According to Ellis's system the geothermal fluids fall into five categories depending on their TKS, pH and the fluid temperature.

Figure 9.7. Picture of a corroded geothermal iron pipe section in contact a bronze valve.

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