

SCALING AND CORROSION IN GEOTHERMAL EQUIPMENT: PROBLEMS AND PREVENTIVE MEASURES

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Abstract—Scale formation and corrosion are major drawbacks in geothermal operations. Although the chemical composition of the geothermal fluids and, hence, corrosion and scaling problems are site-specific, some general rules and recommendations may be given.

A brief summary of the “state of art” in scaling and corrosion prevention techniques is given, with particular reference to ENEL experience.

INTRODUCTION

Geothermal fluids generally contain dissolved gases and solids whose thermodynamic behaviour during the utilization cycle may cause trouble either by attacking the metal surfaces (corrosion) or causing scaling. Before examining the different aspects of these problems let us consider the different thermodynamic conditions of the geothermal fluid during electric utilization. Figure 1 shows that in a double flash geothermal power plant the temperature may vary from as high as 350°C at well bottom to values approaching 60–80°C in the reinjection lines, while pressure may vary from 300 to 0.08 bar.

The geothermal fluid may come into contact with atmospheric air in the condenser and during reinjection. Since the chemical composition of the geofluids varies from almost pure water or steam to hot brine with 360,000 ppm of dissolved solids, we can conclude that scaling and corrosion are very often site-specific and that there is no unique solution. Nevertheless a statistical approach can be attempted and some general rules may hold valid.

SCALING PROBLEMS

Scale formation is one of the main problems in the exploitation of geothermal resources.

It is generally agreed that the four major classes of scaling are: (a) silica and silicates, (b) carbonate and (c) sulphate and sulphide.

Silica is generally in the form of amorphous silica such as opal. Silicates are also amorphous to near-amorphous. Carbonate scales are predominantly low-magnesium calcites although some high magnesium contents and aragonite have been found.

Sulphates are mainly calcium sulphates and barite. Anhydrite dominates at higher temperatures. Sulphides occur in the form of many phases, usually well crystallized. Predominant are Pb, Zn, Fe, Cu while Sb₂S₃ was found in the wells of the Monte Amiata geothermal field.

Mechanism of scale formation

Little is known of the precise mechanism leading to scale formation but we can distinguish three main environments:

- (1) deposition from a single-phase fluid (reinjection pipelines),
- (2) deposition from flashing fluid (wells, separators, two-phase pipelines),
- (3) deposition by steam carry-over (separators, turbines, steam pipelines).

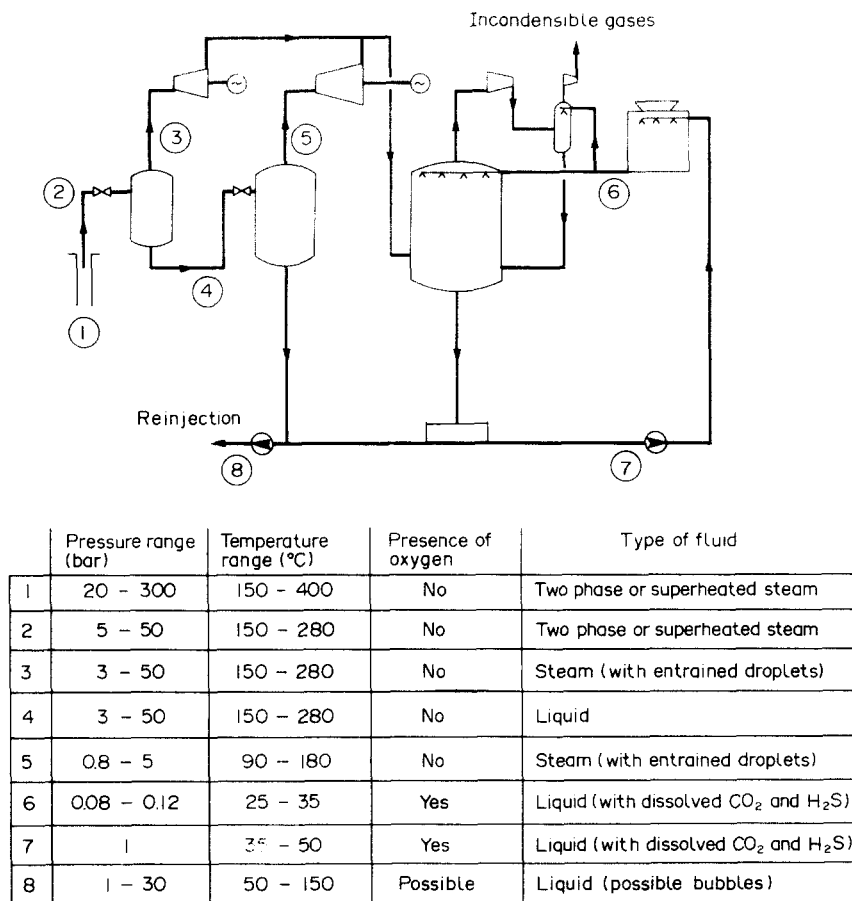


Fig. 1. Typical thermodynamic conditions in geothermal power plants.

Types 1 and 3 are the easiest to understand but probably most scaling phenomena derive from process 2.

Precipitation of solids from a single phase fluid has been studied for many years. The fluid must of course be supersaturated with respect to that phase.

Nucleation and the kinetics of deposition depend strongly on the degree of supersaturation, pressure, temperature and additional catalytic or inhibitory effects, such as the presence of minor elements, the nature of the substrata, etc.

Deposition from flashing fluids is little understood, though it appears to be a major cause of scaling. Flashing is initiated by pressure drops or by cavitation in turbulent flow, and is thought to be responsible for calcite scale. Flashing greatly enhances supersaturation through one of three mechanisms: (a) loss of steam from the liquid phase increases concentrations of the remaining solutes, (b) temperature drop associated with the expansion process, and (c) loss of stable gases such as CO₂ or H₂S increases pH.

Deposition by steam carry-over is responsible for scales on turbines and other components exposed to steam only. This is caused by water droplets carried along and then evaporated on a substratum. Because they are based on complete evaporation, such scales may also contain some of the soluble minerals, such as borates and halites.

CaCO₃ scaling

Almost all geothermal systems contain dissolved carbon dioxide. The amount of CO₂ present

in a water solution at equilibrium is proportional to the partial pressure of the CO_2 in contact with the solution, according to Henry's law.

Figure 2 gives the pressure of CO_2 vs temperature for each ppm of dissolved CO_2 .

The concentration of dissolved CO_2 also includes carbonic acid H_2CO_3 (the trigonal planar structure) which is present as H_2CO_3 and usually represents about 3% of the total. Geothermal exploitation begins with a static CO_2 charged liquid with no vapor phase. When production starts pressure decreases and the equilibrium shifts to the right.

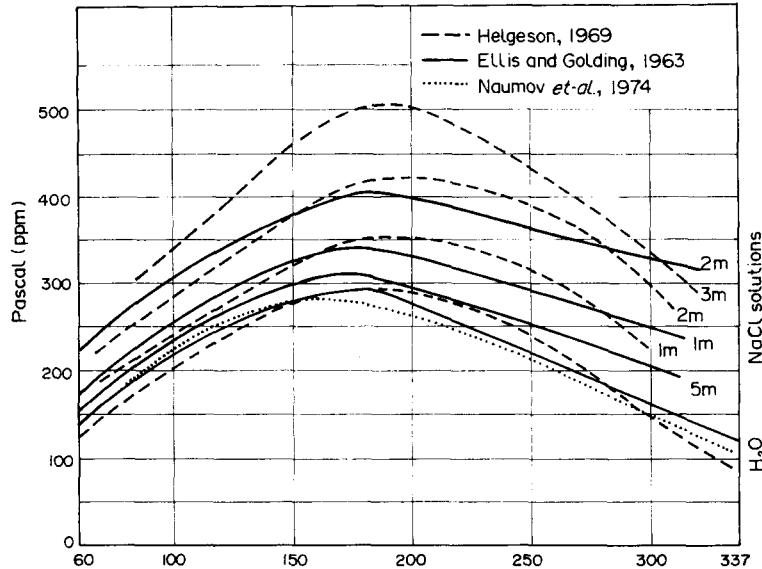
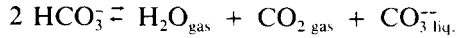


Fig. 2. Pressure concentration for CO_2 vs temperature and NaCl content (from Michels, 1981).



The CO_3^{2-} concentration increases and may cause CaCO_3 precipitation, according to the solubility product $(\text{Ca}^{++}) \cdot (\text{CO}_3^{2-}) = K_p$. Precipitation of CaCO_3 thus begins with flashing. If flashing takes place in the productive well we will have in-hole scaling, if it begins in the formation we will have formation plugging, and if it occurs in the surface equipment the encrustations will be in the surface equipment.

The relationship between the different ionic species may be found from the following equilibria equations

$$\frac{(\text{H}^+) (\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)_{\text{apparent}}} = k_{\text{H}_2\text{CO}_3}$$

$$\frac{(\text{H}^+) (\text{CO}_3^{2-})}{(\text{HCO}_3^-)} = k_{\text{HCO}_3}$$

$$\frac{(\text{H}_2\text{CO}_3)_{\text{apparent}}}{P_{\text{CO}_2} \alpha_c} = k_{\text{CO}_2}$$

$$(\text{Ca}^{++}) (\text{CO}_3^{2-}) = k_{\text{CaCO}_3}$$

where () are the activities, k the equilibrium constants, P_{CO_2} the CO_2 partial pressure and α_c the CO_2 fugacity coefficient.

Rearranging the above equations and putting $P_{\text{CO}_2} = y_{\text{CO}_2} P_T$ and y_{CO_2} being the mole fraction of CO_2 in the gas phase and P_T the pressure, we obtain

$$[\text{Ca}^{++}] = \frac{k_{\text{HCO}_3} \cdot k_{\text{CO}_2} \cdot y_{\text{CO}_2} P_T \alpha_c}{k_{\text{HCO}_3} \cdot (\text{HCO}_3^-)^2 \cdot \gamma_{\text{Ca}^{++}}}$$

where $\gamma_{\text{Ca}^{++}}$ is the Ca^{++} activity coefficient.

Since alkalinity Alk is mainly given by HCO_3^- concentration in geothermal waters, the above equations show that calcium ion concentration $[\text{Ca}^{++}]$ depends upon temperature, CO_2 partial pressure and ionic strength I . It is thus possible to define the saturation index I_s (Oddo, 1982), the ratio between the measured Ca^{++} concentration and the Ca^{++} concentration in equilibrium conditions as:

$$I_s = \log F_s$$

where

$$F_s = \frac{[\text{Ca}^{++}] \text{Alk}^2 k_{\text{HCO}_3} \gamma_{\text{Ca}^{++}} \gamma_{\text{Alk}}^2}{k_{\text{HCO}_3} k_{\text{CO}_2} P_{\text{CO}_2} \alpha_c}$$

Since the equilibrium constant can be expressed as a function of temperature and of ionic strength I we have

$$I_s = \log \frac{[\text{Ca}^{++}] \text{Alk}^2}{P_T \cdot y_{\text{CO}_2}} + 10.22 + 2.739 \cdot 10^{-2} T - 1.38 \cdot 10^{-5} T^2 - 1.079 \cdot 10^{-8} P_T - 2.52 I^{\frac{1}{2}} + 0.919 I$$

where I , $[\text{Ca}^{++}]$ and Alk are expressed as moles/litre, P_T as Pascal and T as $^{\circ}\text{C}$.

Of course $I > 0$ indicates a supersaturated scaling solution and $I < 0$ an undersaturated solution.

By measuring Alk, $[\text{Ca}^{++}]$ concentration and CO_2 content it is possible to predict calcium carbonate scaling behaviour in any point of the utilization cycle. Unfortunately reliable downhole sampling is quite difficult to achieve and bad sampling can produce misleading results.

Prevention of CaCO_3 scaling

Effective scale prevention in geothermal operations is often critical to the success of a project. Unfortunately scale prevention methods must be designed and tailored to the very site-specific conditions in the field. These conditions dictate the type of scale prevention method that will be feasible.

Calcium carbonate scaling may be prevented by:

- (1) acting on CO_2 partial pressure,
- (2) acting on the pH of the solution,
- (3) using chemical additives (scale inhibitor).

CO_2 partial pressure control

Pressure and temperature manipulations of the geothermal fluid can be achieved quite easily by pumping a geothermal well instead of relying on its natural flow. Utilizing a down-hole pump

will drastically decrease or eliminate the in-hole pressure and temperature drops caused by flashing.

The produced fluids can be maintained as a single phase system by means of a mechanical downhole pump. Thus, the formation of "pressure sensitive" scaling such as CaCO_3 can be eliminated. The formation of "temperature sensitive" scaling such as BaSO_4 can be retarded or at least shifted from the wellbores into the more accessible surface equipment where their handling becomes much easier.

Unfortunately, the use of downhole pumps is restricted somewhat by the fluid temperatures. At present, no downhole pump is guaranteed to work at wellbore temperatures in excess of approximately 190°C .

Another potential scale prevention method consists in artificially maintaining a high CO_2 partial pressure by re-injecting some of the produced CO_2 back into the producing well according to the scheme of Fig. 3.

Experiments on this method were successful in the USA (Kuwada, 1982) but it appears valid only for fluid with low CO_2 partial pressures.

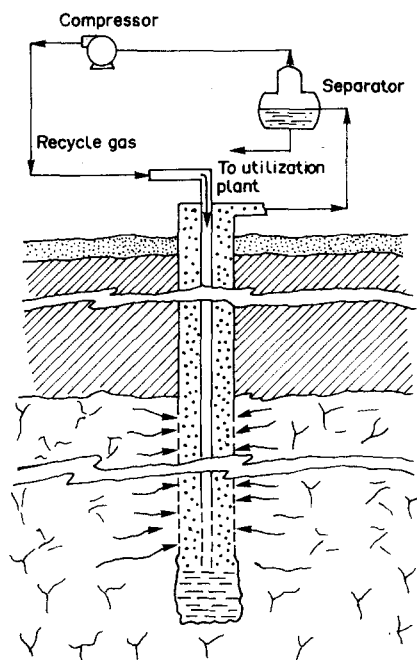


Fig. 3. Sketch of a plant for CO_2 partial pressure control.

pH manipulations

Manipulation of the chemical composition of the geothermal fluids, particularly their pH, is another potentially valuable way to avoid scaling. However, the cost of such a process is often overlooked. For example, adding HCl to a geothermal fluid in order to decrease the pH below a certain value at which no CaCO_3 scaling can form may be technically but not economically feasible. The cost of the acid may be much higher than the cost of the electricity produced from the system, since many geothermal liquids have an extremely large buffer capacity. Excessively large amounts of acid are then required to obtain even fairly small decreases of pH.

For instance experimental tests in Torre Alfina showed that 200 cm^3 of HCl 0.1 N were required for each litre of solution to avoid CaCO_3 precipitation.

Chemical scale inhibition

The utilization of scale inhibitors is the most common and promising method of combatting scaling problems in oil and gas field operations. Problems occur when extending this technique to geothermal operations because of the high temperature and salinity of the brines.

The main problem is to select the most suitable inhibitor among the hundreds of different chemicals on the market.

A selected list of inhibitors is shown in Table 1. Some of these inhibitors have been tested in field operations in Italy (Corsi *et al.*, 1985).

Table 1. Calcium carbonate scale inhibitors utilized in laboratory tests

Additive	Manufacturer	Chemical-type
Dequest 2060	Monsanto	organophosphonic acid
Dequest 2066	Monsanto	organophosphonic acid
Ecostabil 4001	Montedison-Arca	organophosphonic acid
Ecostabil 4004	Montedison-Arca	organophosphonic acid
Ecostabil EP/85	Montedison-Arca	organophosphonic acid
Ecopol 4014	Montedison-Arca	polyacrylamide
Ecopol 4022	Montedison-Arca	polyacrylamide
Nadar 4053	Nadar	organophosphonic acid
Nadar 4054	Nadar	organophosphonic acid
Flocon 247	Pfizer	polycarboxylic acid
Chelone DPNA	Eurosyn	organophosphonic acid
Sequion 40 Na 32	Bozzetto	organophosphonic acid
Procedor ST 90	Procedo	blend
Sodium Fumate	Mitsubishi	...

These inhibitors were tested in the laboratory before application in the Cesano and Latera fields (Corsi *et al.*, 1985): the best results were obtained with the organic phosphonates such as Dequest 2066 and Sequion 40 Na 32; the main conclusions of the work carried out so far can be summarized as follows:

- the presence of dissolved salts and some trace elements (Mn, Fe, As) does not affect product effectiveness
- the inhibitor is also effective when injected in a two-phase flow with nucleation already initiated
- phosphonates maintain their effectiveness until 180–200°C; some results show a partial degradation of the product after treatment at 210°C, so that double concentration has to be used to obtain the same inhibiting action
- the inhibitors maintain their effectiveness for some hours so that reinjection can continue without trouble. The problem of injecting the inhibitors down-hole was overcome by setting up the plant schematically represented in Fig. 4.

This consists basically of a small incoloy pipe (4.76 mm) that can be lowered into the well to inject the inhibitor.

This system was used in the Cesano (Cesano 1 well) and Latera geothermal fields, producing very satisfactory results both technically and economically. For instance it was found that 4 ppm of inhibitor were sufficient to avoid scaling in Latera 3D well, which feeds a geothermal back-pressure power-plant. Well Latera 3D, at a flow rate of 600 t/h, is, in fact, capable of producing approximately 15 MWe with a double-flash condensing power plant. At a concentration of 4 ppm, the economic impact of the inhibitor is 0.16 mills/kWh (1985), which is fully acceptable. On an annual basis, the cost of the inhibitor can be quantified at about ¼ of the cost of a single well reaming.

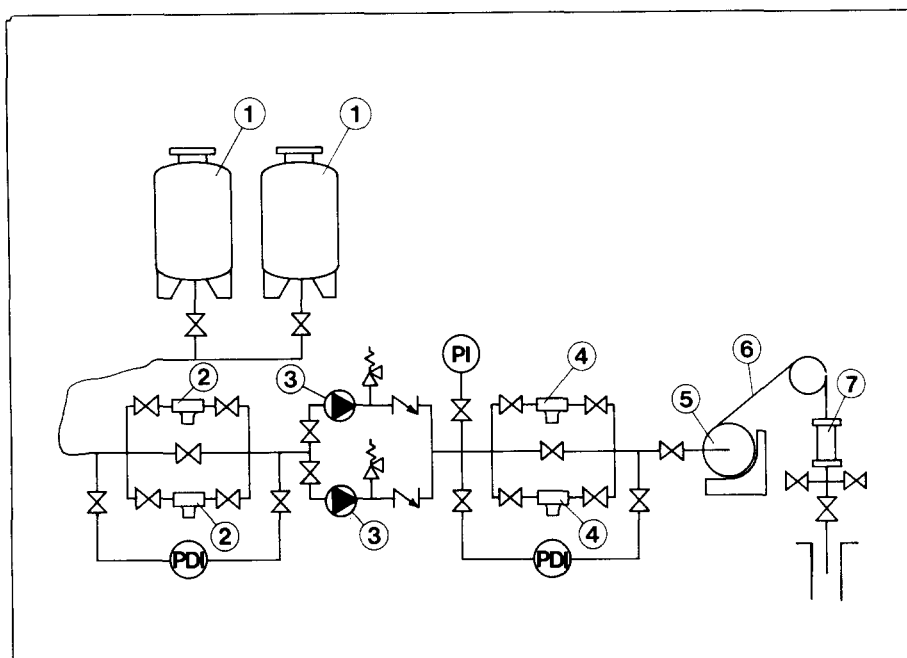


Fig. 4. Simplified scheme of the downhole inhibitor injection equipment. (1) inhibitor tanks, (2) low-pressure filters (60 μm), (3) metering pumps, (4) high pressure filters (20 μm), (5) tube drum and winch, (6) incaloy tube, (7) stuffing box.

Silica scaling

While CaCO_3 scaling in medium temperature resources occurs mainly in production wells and high temperature equipment, silica scaling is very frequent in plants using steam flashed from high temperature resources, especially in the reinjection lines, separators and sometimes in the wells (Fig. 1).

The behaviour of silica SiO_2 in aqueous solutions has been widely studied and reported (Fournier and Marshall, 1983; Ellis and Mahon, 1977). The two forms of silica that are relevant to our problem are quartz and amorphous silica. Generally in the geothermal reservoir we assume that the fluid is in equilibrium with quartz at the temperature of the fluid. Over the range of interest for geothermal applications the amount of quartz that dissolves in the fluid increases with temperature and decreases with salinity (Fig. 5). Over the range of interest ($\text{pH} < 8$) the solubility of quartz can be considered independent of pH.

As it is cooled, the geothermal fluid becomes supersaturated with respect to quartz. Fortunately the kinetics of quartz is very slow and silica deposition at lower temperatures is controlled by the equilibrium of amorphous silica, which is more soluble than quartz at a given temperature (Fig. 5). Thus the potential for silica precipitation exists only at temperatures below the appropriate saturation temperature for the equilibrium solubility of amorphous silica. Amorphous solubility increases with temperature, decreases with salinity and increases sharply with pH. The rate of deposition of amorphous silica seems to be controlled by the rate of polymerization of monomeric silica.

The kinetics of silica polymerization are complex, and the rate depends on both the degree of supersaturation and temperature. The reactions may be chain reactions catalyzed by chloride and hydroxide. Sodium ions, potassium ions and sulphate ions have little effect (Ellis and Mahon, 1977).

Because the kinetics of scale deposition are slow at ambient temperatures, the location of the siliceous scale is dependent on residence time of the supersaturated fluid. Studies have shown

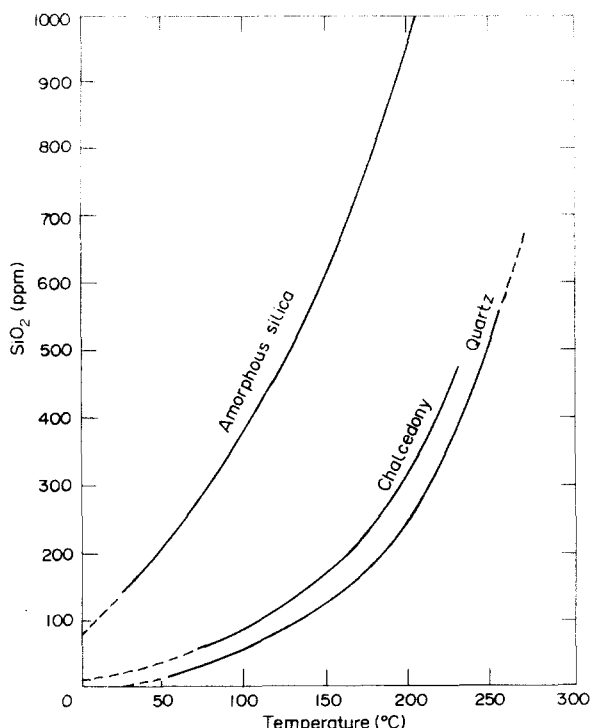


Fig. 5. Silica solubility vs temperature.

that acidification slows the rate of precipitation. Acidification of Salton Sea fluid (pH 5–6) to pH 4.5 delays precipitation for at least three months. At pH greater than 8, ionization of silica occurs, which greatly increases the solubility of silica.

Prevention of silica scaling

From the above considerations it would seem that in principle the pH of a solution can be varied to reduce or eliminate silica scaling.

This method was tested in Mexico and the USA by adding either HCl or NaOH to the geothermal brine. In both cases the results were encouraging, but the cost of the reactives were very high and a new approach should be attempted.

Tests carried out in Italy on silica scaling inhibitors gave very promising results during lab tests: a method to simulate silica precipitation was set up (ENEL-UNG – Final Report 1985) and many inhibitors were tested. Among these, a new product was able to prevent silica precipitation from supersaturated solution. Unfortunately these encouraging results were not confirmed in the field tests carried out in the Mofete geothermal field and further work is necessary.

Scaling inhibitors were also tested in the USA and Mexico, but for the moment there is no known and economically feasible inhibitor for the very problematic silica, silicate and heavy metal sulphide precipitations. In addition, pressure, temperature and flow rate manipulations will allow the operator to shift the locations of these scales within the equipment but will not allow him to eliminate his scale problem.

Scale treatment

Where chemical additives are not effective a totally different technique to combat the scale problem can be tried. Instead of attempting to prevent the formation of scale, it is possible to

allow deposition of the scale within specially designed equipment by carefully choosing the incremental steps in reducing the pressures and temperatures between the wellheads of the producing wells and those of the injection wells.

Numerous types of equipment can be used for this technique, depending upon the total pressure and desired pressure drop at any given location. For example, if the scaling problem is located in the flash tank, a special flash crystallizer may be erected (Vetter and Kandarpa, 1982).

Figure 6 shows schematically the principle of a flash-crystallizer as described by Vetter and Kandarpa (1982), "the basic principle of a flash-crystallization process is that the brine is suddenly flashed from non-scaling to scaling conditions and, at the same time, enough seed for the precipitation reactions is provided so that the precipitating solids do not grow on the internal walls of the equipment but on the provided seed. Thus, a large internal surface area must be provided within the liquid through seed addition (suspension) to avoid the competitive growing of solids on the walls. Growth of scale on the walls is caused by a different type of seed either provided by the walls themselves or by some of the added seed adhering to the walls. This principle flash-crystallization through seed addition and simultaneous flashing boils down to a complex control of numerous and often competitive precipitation reactions which are governed by the thermodynamics and kinetics of each reaction and the hydrodynamics in this system".

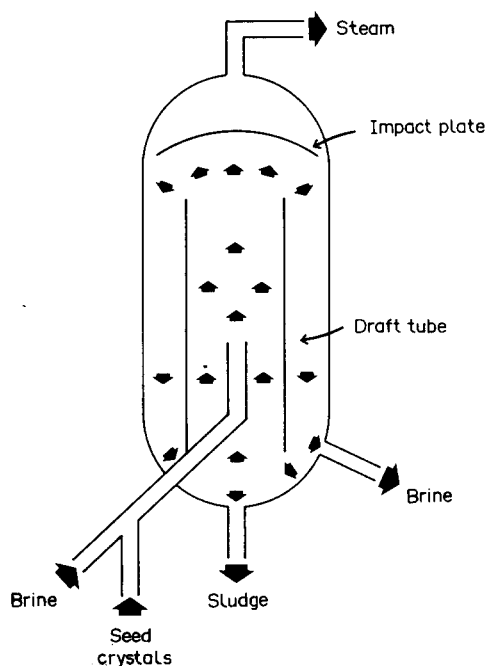


Fig. 6. Principle of flash crystallizer (from Vetter and Kandarpa, 1982).

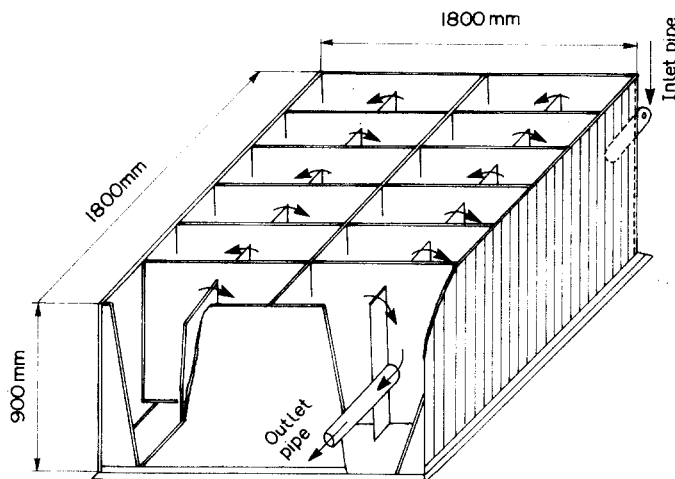
Of course this type of approach does not solve the problem of reinjection pipeline, where, because of the temperature drop, suspended silica particles may be present. In these cases the conventional approaches of water clarification can be tried. These consist basically of solid – liquid separations such as sedimentation flotation, filtration or cyclone separation as described in Unit Operation Books. The large flowrates involved in geothermal operations make the use of these methods problematic because of the size of the purification plants required. In any case, Table 2 shows a list of possible solutions.

Each of the afore-mentioned treatments still presents the same drawback: a solid product requiring disposal, and this appears to be the main obstacle for industrial use of this type of

Table 2. Possible solutions for downstream silica removal

Type of treatment	Hydraulic load ($\text{m}^3/\text{m}^2 \cdot \text{h}$)	Drawbacks
Sedimentation (thickening + clarification)	1–2	Hydraulic and convective turbulence
Flotation	10–15	Partly affected by convective motion
Filtration	0.5–1	Expensive
Sand filtration	10–15	Not suitable for high suspended particles concentrations
Hydrocyclones	> 100	Low efficiencies and breakdown of flocculates

treatment. As an example of the latter, we might mention the retaining tank used in Japan (Fig. 7). The exhaust brine flows through the tank for a sufficient time to allow deposition of silica on the diaphragms, which are periodically cleaned.

Fig. 7. Experimental retaining tank (from Yanagase *et al.*, 1970).

Unfortunately this simple method cannot be generalized since the kinetics of silica precipitation depends upon the site-specific composition of the brine.

CORROSION IN GEOTHERMAL UTILIZATION CYCLES

Generally speaking we can find all the different forms of corrosion in geothermal equipment and it appears useful to recall the main characteristics of each:

Uniform (or general) corrosion

A general all-over attack of the metal surface that is transformed into “rust”. Uniform corrosion is often promoted by chloride, ammonia species, or hydrogen ions.

Pitting

A localized form of attack in which pits develop in the metal surface. Pitting is often associated with the breakdown of a passivation film or surface scale. Initiation and penetration rate of pits are unpredictable.

Crevice corrosion

Similar to pitting in that it is a localized attack. Unlike most other forms of corrosion, it is geometry-dependent, occurring in fabrication crevices of equipment or under scale deposits.

Stress corrosion cracking (SCC)

A catastrophic type of failure promoted by a combination of stress and the presence of chloride ion in the environment. The presence of oxygen and increasing temperatures increase the severity of attack. SCC is the most dangerous form of corrosion in the geothermal environment.

Sulphide stress cracking (SSC)

Catastrophic failure of high strength steels exposed under stress to environments containing H_2S in an aqueous phase. In contrast to stress corrosion cracking, the severity of SSC decreases with increasing temperature and oxygen has little, if any, effect. Although, low pH greatly accelerates failure, SSC is more typical of the oil industry than geothermal because of the high temperature of the geofluids.

Hydrogen blistering

This form may occur in low strength steels exposed to aqueous solutions containing H_2S . Ruptures may occur when hydrogen trapped in voids accumulates at a sufficient pressure. The material need not be under stress for hydrogen blistering to occur.

Intergranular corrosion

Severe localized corrosion at or adjacent to grain boundaries, with little or no attack on the bodies of the grains. The alloy disintegrates (grains fall out) and/or loses its strength. Intergranular corrosion results from improper heat treatment.

Galvanic coupling

This occurs when two dissimilar metals are electrically connected. The less noble material will be attacked. Materials may be ordered in a galvanic series (by increasing nobility) to help in material selection. Care must be taken since the order of metals may change depending upon the chemical composition of the environment in which the metals are immersed.

Corrosion fatigue

Occurs when cyclic stresses are imposed on a material in a corrosive environment. The corrosion fatigue limit is the greatest unit stress that may be applied under given conditions of stress, rate of stress application, temperature and corrosive environment without causing it to fail in a given number of cycles of stress. The combined effects of cyclic stress and corrosion are often far more severe than the simple sum of their actions.

Erosion corrosion

Accelerated metal loss caused by impingement of high velocity fluid, droplets, or particulates. Erosion corrosion can be serious in the wet end of turbines or at sites of two-phase flow.

Cavitation

Accelerated local corrosion promoted by the formation and collapse of vapor bubbles near a metal surface.

Corrosion rate measurements

The selection of the material to be used in geothermal equipments may be a very difficult problem considering all the afore-mentioned forms of corrosion occurring in geothermal installations. Experience is often the only valid method for selecting materials. Unfortunately the chemical composition of the geothermal brine may vary and it is difficult to find general guidelines.

Although the solutions may not always be totally reliable, corrosion rate measurements are often the only guide the technician has in the selection of equipment materials.

Uniform corrosion rate: weight loss measurement

A clean sample (Fig. 8) of the test metal is measured, weighed, exposed to a corrodent for a known time, removed, cleaned to remove corrosion product and reweighed. The rate of metal removal due to corrosion is then calculated from:

$$R = \frac{KW}{ATD}$$

where R is the corrosion rate, T is the time of exposure in hours, W is the weight loss in mg (corrected for any loss during cleaning), A is the area to nearest cm^2 and D is the density in g/cm^3 . If R is expressed in mm/yr , then the constant K is $8.76 \cdot 10^4$. With this method, coupled with a naked eye assessment of shape and number of pits, pitting corrosion can also be estimated. It must be remembered that the indications from this type of measurements are valid only for uniform corrosion rate. No information is given on the other forms of corrosion.

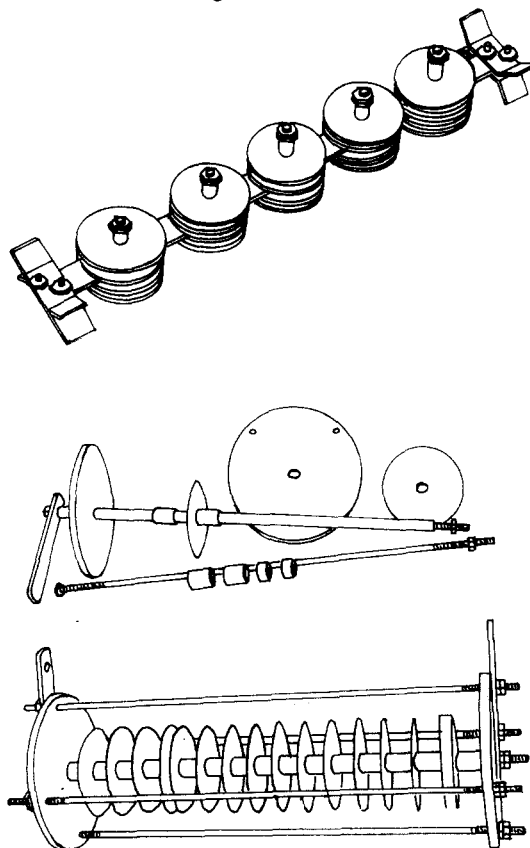


Fig. 8. Assembly of corrosion test spool and specimen.

Stress corrosion cracking: stress corrosion test specimen

SCC can be measured by means of stress corrosion test coupons of various shapes. A typical C-ring specimen is shown in Fig. 9. The specimen, according to the ASTM G38 standard, must be obtained from bars or sheets (Fig. 8). Their thickness shall never be less than 6 mm. The test is carried out on materials charged to a value of $R_{p0.2}$ * and to 70% of $R_{p0.2}$ as the resulting evaluation will be comprehensive of normal working conditions and eventual material stress.

After exposure to the corroding fluid, the specimen will be analyzed metallographically according to very accurate specifications. The tests are hence very long and expensive, especially for C-ring preparation and analysis.

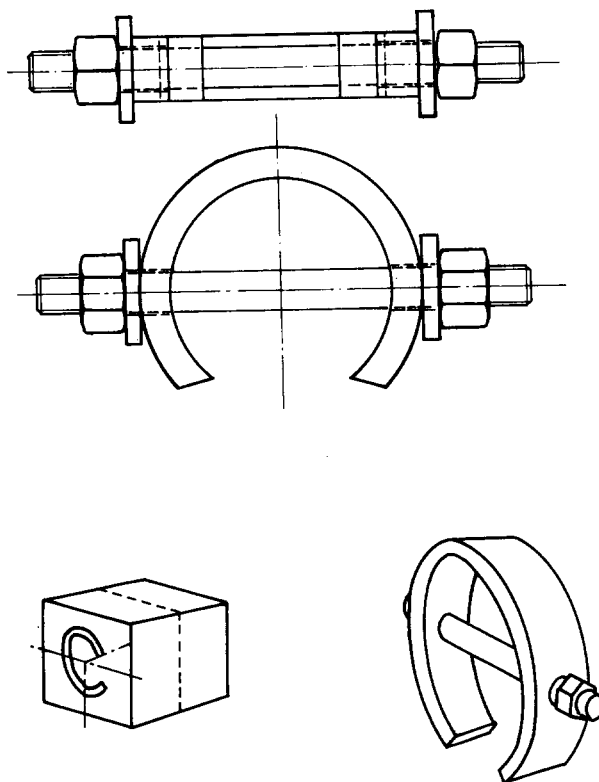


Fig. 9. Stress corrosion test specimen: the C-ring.

SCC and uniform corrosion rate measurement: the electrochemical test method

This method is based on the study of the curve potential – current of polarization. The apparatus generally used is sketched in Fig. 10.

A potenziostat is generally used to determine anodic polarization behaviour. Generally the metal to be tested is:

- (1) cleaned and put into a polarization cell,
- (2) metal is allowed to come in its natural freely corrodent state,
- (3) potential is changed by using the external circuit in the noble direction. It is kept at this potential long enough for equilibrium conditions to be reached,

*The stress at which permanent strain is 0.2%.

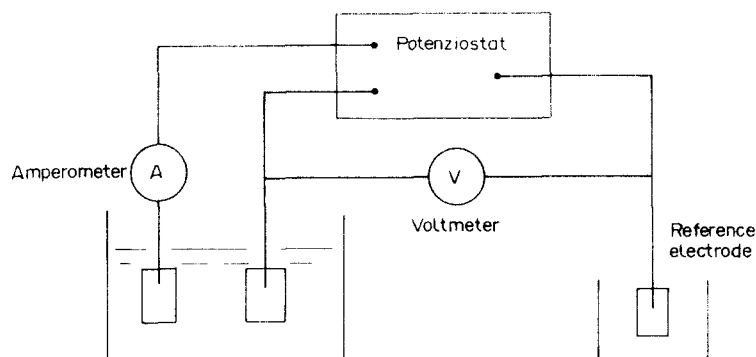


Fig. 10. Sketch of an electrochemical apparatus.

(4) current flowing in external circuit is measured and the procedure is repeated. The result is a curve like that shown in Fig. 11.

The electrochemical measurements are used on a wide scale in the evaluation of corrosion, both in the laboratory and the plants; these data are used to evaluate corrosion rate approximately, repassivation rate in geothermal environments, as well as to define the materials subjects to SCC.

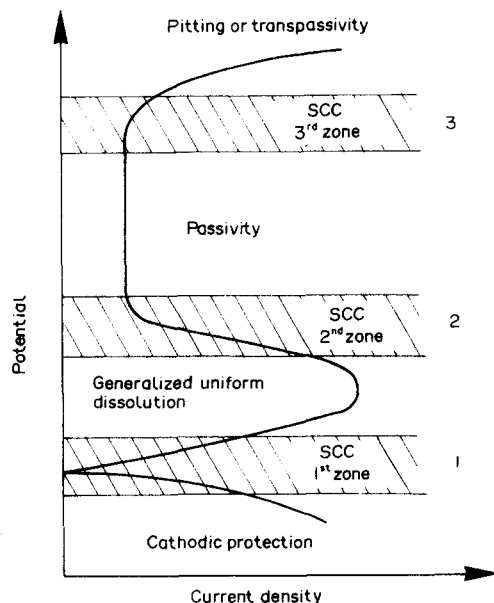


Fig. 11. Sketch of potential vs current density showing the zones of SCC inception.

The electrochemical measurements, on the other hand, will give information on the behaviour of the materials in the test environment over sufficiently short periods.

Figure 11 shows a potentiodynamic curve with the potential ranges in which SCC is theoretically liable to occur.

The electrochemical measurements can be also carried out as field measurements, but special electrodes and equipment capable of resisting temperatures of $\sim 200 - 250^\circ\text{C}$ and pressures of 20 – 25 bar are necessary.

CORROSIVE SPECIES IN GEOTHERMAL FLUIDS

Geothermal fluids contain several chemical species that have a significant effect on the corrosion of metallic construction materials. These key species, which were identified from corrosion

literature and data on chemical composition of fluids from liquid-dominated geothermal resources, are as follows:

- oxygen,
- hydrogen ion (pH),
- chloride ion,
- hydrogen sulphide,
- carbon dioxide species,
- ammonia species,
- sulphate ion.

A quantitative prediction of their corrosive effects is complicated by the following factors:
—different materials respond to the same fluid component in different ways and to different degrees;

—the interaction of two or more chemical species may give different results from those obtained with the individual species;

—the importance of a species depends on the form of attack (uniform corrosion, pitting, crevice corrosion, stress corrosion, cracking, or corrosion-fatigue).

Other components that are less common or aggressive can also produce corrosive effects in some geothermal fluids. Examples are fluoride ion, heavy metals, and boron.

A complete review of the corrosive effects of some species is reported in Ellis and Conover (1981).

The general rules are summarized in the following:

Oxygen

Dissolved oxygen is the most serious contaminant of geothermal fluid steam and condensate. Aerated geofluid causes a tenfold or greater increase in the uniform corrosive rate of carbon steel. Together with the chloride ion, at a certain temperature oxygen can initiate SCC failure. A few materials, especially aluminium alloys, require dissolved oxygen to maintain their passivation films. These alloys corrode in oxygen-free geothermal fluid. As shown in Fig. 1, oxygen is generally present at low temperatures where it may not be so dangerous. It is very important to avoid oxygen contamination in the reinjection lines where the temperature may increase when the fluid flows in the injection wells.

Hydrogen ion

The corrosion of carbon and low alloy steels is generally controlled by pH. The corrosion rate of these steels decreases as pH increases. Since the passivity is often pH-dependent, the corrosion resistant alloy may also be subjected to pitting, SCC etc, in low pH solutions.

Chloride ion

The uniform corrosive rate is greatly enhanced by the presence of the chloride ion. At low temperatures and for concentrations of up to 100,000 ppm it has been demonstrated that uniform corrosion rate is proportional to the square root of chloride concentration.

Chloride ion also induces a breakdown of passivity of passivated alloys and stress corrosion cracking in austenite stainless steel. Five to ten ppm may be sufficient at temperatures higher than 50°C to promote SCC in AISI 316 stainless steel.

Chloride ions are extremely mobile and can concentrate to near saturation in pits or crevices. For this reason the chloride concentration of the bulk fluid may be misleading.

Hydrogen sulphide

Perhaps the most severe effect of hydrogen sulphide is its attack on certain copper and nickel alloys, especially cupronickels and other copper alloys containing nickel, as well as Monels. These

metals have performed well in seawater but are practically unusable in geothermal fluids containing hydrogen sulphide. The threshold of attack is less than 30 ppb hydrogen sulphide and copper or silver electrical contacts fail in the presence of this atmosphere.

The effect of H_2S on steels is less predictable. High strength steels are often subject to SCC at low temperatures. Oxidation of H_2S in aerated waters can decrease pH and increase corrosiveness.

Carbon dioxide species

Dissolved carbon dioxide occurs naturally in many geothermal fluids and has a major corrosive effect on carbon and low alloy steels. Carbon dioxide is one of the most important species in the control of the pH of geothermal fluids. In many cases, the low pH resulting from carbon dioxide dissolved in condensed steam is the factor controlling corrosion of geothermal steam lines. Increasing the partial pressure of carbon dioxide reduces the pH of solutions.

Theoretical considerations show very high uniform corrosion rate in presence of CO_2 and sodium chloride until about $80^\circ C$. Above $80^\circ C$ stable iron carbonate films are formed which slow the corrosion rate compared to predicted values.

Other species

Among the other species the most important is ammonia: it may cause SCC in some copper alloys and may affect the pH of cooling water.

Heavy or transition metal ions may be corrosive if present as oxidized forms, but generally in geothermal fluids they are present in the lowest oxidation state. They can play the same role as a catalyzer.

Sulphate ion is generally present in geothermal waters but rarely causes the same severe localized attack as chloride, which is always present.

ITALIAN EXPERIENCE

From what has been said previously it can be concluded that a knowledge of the chemical composition of the geothermal fluid is vital to predict the behaviour of materials in the geothermal environment.

Nevertheless some simple general considerations can be attempted on the basis of experience and considering the following general characteristics of the geothermal fluid:

- most of the water-dominated geothermal resources contain 500–16,000 ppm of dissolved solids;
- chloride constitutes at least 45% of the total T.D.S.;
- uncondensable gas represents less than 5% of the reservoir fluid. Most of the gas is CO_2 ;
- H_2S and NH_3 are present in low percentages;
- the pH of unflashed fluid is between 5 and 7;
- the fluids of steam-dominated geothermal resources contain 50–300 ppm of H_3BO_3 , 3–30 ppm of chloride ion, 50–150 ppm of ammonia, 50–500 ppm of H_2S and 10,000–20,000 ppm of CO_2 .

A brief review of the Italian experience is reported below.

Materials of well, piping and separators (temperature $150–350^\circ C$):

There is no metallic material capable of being free of corrosion in these extreme conditions.

Experience shows that only some very expensive austeno-ferritic or super austenitic alloys can resist corrosion attack. On the other hand, austenitic stainless steels (AISI 304 or AISI 316) are susceptible to stress corrosion with temperatures higher than $60^\circ C$ and chloride concentrations higher than 5–10 ppm.

Copper or aluminium alloys also gave poor results because of the presence of H_2S . Since plastic materials are generally not suitable in high temperature environments there is, for the moment, no economic alternative to the use of carbon steel for high temperature piping and separators. In this case, corrosion rate should be measured to indicate the necessary overthickness due to corrosion.

Reinjection piping

If the reinjection pipelines are maintained at a temperature higher than $\approx 120^\circ$ the previous considerations are still valid. If reinjection is carried out at low temperature after flashing to the atmosphere, fiber glass pipelines can be considered a valid alternative.

Thermal and hydraulic machinery

Selection of this material is complicated, in addition to the normal strong mechanical stress, by the need to cope with corrosion-erosion due to high velocity fluid.

In addition, scaling can occur anywhere in the turbine. As a general rule martensitic stainless steel such as AISI 403 gave good results for the blades, while alloy steels may be used for the rotors and casing. There are some particular types of geothermal steam, containing more than 30 ppm of chloride ions, that present very aggressive characteristics. In these cases, catastrophic blade failures may occur and alternative materials or solutions must be studied. Since 1956 the steam has been washed in Italy by introducing in the pipeline alkaline solutions that retain the acid soluble component of steam, separating the liquid downstream in separators.

This solution avoided failures and very fast uniform corrosion rate but is expensive (about 3.5% of electric production is lost due to the desuperheating of steam and the pressure drop).

To avoid this loss, some tests were carried out in Italy to find alternative materials for the blades and rotors of the turbines. An experimental plant consisting of a small heat exchanger was installed to simulate the "dew point", i.e. the conditions (pressure, temperature, chemical composition) existing in the turbine when the first drop of liquid is formed. Prestressed samples of various test materials were inserted in the heat exchanger in contact with condensing steam. After an exposure time of 2 months the samples were extracted and examined with the methods described in *Corrosion Rate Measurements*.

The results were not encouraging: only titanium alloy and some super-austenitic alloys such as AVESTA 254 SMO gave satisfactory results. As a consequence some titanium blades were inserted in existing turbines in the dew point region to further test the material, but it was decided for the moment to maintain steam washing where the steam contains high chloride ion percentages.

Where the chloride ion concentration is not high (less than 65 ppm) the new types of materials such as UNI X5 Cr Ni Mo 126 for the rotors and AISI 403 for the blades are considered adequate.

The stems of the turbine-regulating valve are coated with ceramic material to avoid corrosion.

As far as condenser and cooling water circuit are concerned, experience shows that carbon steel undergoes a fairly rapid and general corrosion since it is easy to depolarize. The use of AISI 316 solved the problem definitively. Fiber glass may also be used for pipelines and some test pieces are installed in Italian geothermoelectric power plants.

Since normal grey cast iron is not reliable, the use of nickel cast iron such as ASTM A439D-2B is recommended for the body of large diameter valves in the cooling water circuit. The inner parts of the valves susceptible to corrosion-erosion may be in AISI 316.

The body of the cooling water circulation pump should be in ASTM A439D-2B while the inner parts of the pump, such as the impeller, are in AISI 316.

Depending on production technology, the diffusers are made of AISI 316 or nickel cast iron.

Buildings in the plant hydraulic circuit

Italian experience showed that in some parts of the buildings made of concrete (cooling towers, barometric well, tunnel), a catalytic oxidation of sulphides to sulphates takes place and the

sulphuric ion attacks the calcium of cement. This attack appears to be promoted by sulpho-reducing bacteria. While studies are being carried out to prevent this type of corrosion, cooling towers made of wood and protective plastering are generally used with satisfactory results.

Electrical equipment

H₂S causes rapid failure of silver or copper contacts. A solution to this problem was found by using gold-coated contacts.

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