# PREVENTIVE METHODS FOR SCALING AND CORROSION IN GEOTHERMAL FIELDS

Baran Kaypakoğlu, Mehmet Şişman, Niyazi Aksoy

baransmail@gmail.com

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## ABSTRACT

This paper emphasizes on the methods to overcome the difficulties of handling geothermal brine during the production process and is based on the experiences gained during the management of a field in the Menderes Massif in Western Turkey. The field is used for electricity generation which has an installed capacity of 17 MW and consists of two more power plants under construction each with a capacity of 23 MW.

Risk of $CaCO_3$ scaling in the production and $SiO_2$ scaling in the reinjection sector is always present during electricity generation process. Prevention of scaling and corrosion is crucial in order for these power plants to function properly, in fact to function at all. The paper mainly covers the tests conducted for the selection of the proper chemicals to prevent scaling and corrosion mentioned above, the mechanisms used for the injection of these chemicals and the management of the field during production.

## 1. INTRODUCTION

### 1.1 Menderes Metamorphic Massif

The largest( in size and output) regional heat flow anomaly in Turkey is found in the Menderes Metamorphic Massif. Several recent grabens have developed within the MMM, where all the geothermal fields are of medium-to-high enthalpy, with temperatures in the 120-240˚C range.

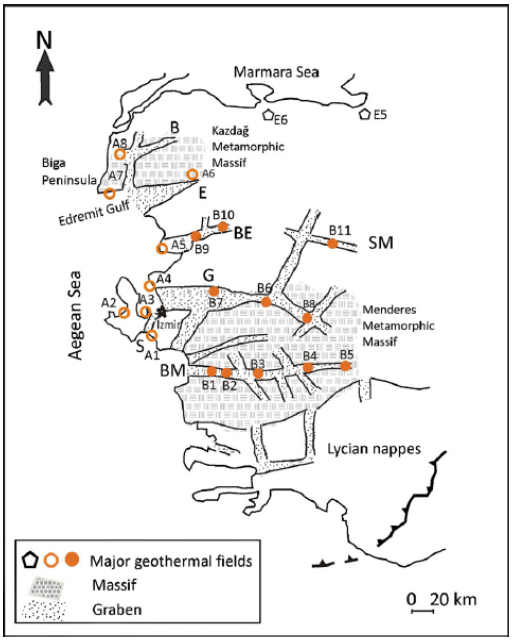

**Figure 1 – Menderes Metamorphic Massif**

### 1.2 Germencik Field

Germencik lies on the south west of the MMM. It is a medium enthalpy field with temperatures ranging between 140-180˚C. The reservoir consists of 20% of steam and 80% of Na-Cl-$HCO_3$ type brine and the brine is highly saturated in respect to calcite.

### 1.3 Irem Power Plant

Irem power plant's construction was finished in September 2011 and the plant started operating in November 2011. It is a binary cycle, integrated two level unit with a design temperature of 160˚C. It's design capacity is 17,5 MW for an ambient temperature of 18˚C. The plant uses Pentane, a hydrocarbon($C_5H_{12}$) as the secondary fluid.

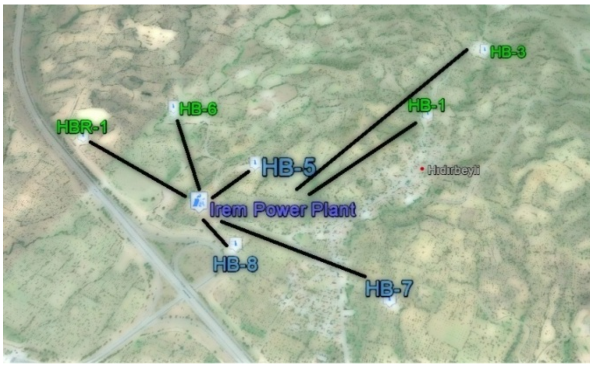

**Figure 2: Irem Power Plant; blue wells are production, green wells are reinjection wells.**

The plant has 3 production and 4 reinjection wells. Each production well has its own individual wellhead seperators and the seperation is done in 10 bars of absolute pressure. After then the steam and brine is gathered in the power plant by seperate pipelines.

## 2. SCALING IN GEOTHERMAL SYSTEMS

Geothermal brine is saturated with various minerals which may form various deposits. Saturation of any mineral in water is mainly dependent on temperature, pressure and pH. Any change in these variables may lead to precipitation of minerals.

### 2.1 Calcite Scaling

Brine, when undisturbed, is in equilibrium state under high pressure and temperature in the reservoir. But when a well is opened for production, brine loses its pressure on the way up and thus loses its equilibrium. The equilibrium reaction is given as follows:

$$CaCO_{3,solid} + CO_{2,liquid} + H_2O \Leftrightarrow Ca^{+2} + 2HCO_3^- \qquad (1)$$

Loss in pressure causes the dissolved $CO_2$ in water to flash into vapor. This decline in $CO_2$ causes the reaction no (1) to show a tendency to the left side and thus will result in $CaCO_3$ precipitation. Calcite, aragonite and vaterite are mineral forms of $CaCO_3$. Vaterite is not very stable and turns into calcite. Eventually, calcium carbonate precipitates as calcite and aragonite.

Dissolved $CO_2$ in water undergoes a number of important inorganic equilibrium reactions effecting the scaling potential of the brine directly and indirectly. First of all it can dissolve limestone as can be seen in equation no (1). Secondly in can react with water to form carbonic acid;

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)} \qquad (2)$$

Carbonic acid may loose up to two protons through acid equilibria;

$$H_2CO_3(aq) \leftrightarrow H^+(aq) + HCO_3^-(aq) \qquad (3)$$

$$HCO_3^-(aq) \leftrightarrow H^+(aq) + CO_3^{-2}(aq) \qquad (4)$$

In both cases the proton is liberated to the water and eventually decreases pH.

If we rewrite the reaction no (2) in the following form we may see the effect of $CO_2$ removal, on pH:

$$CO_{2(aq)} + H_2O = H^+ + HCO_3^- \qquad (5)$$

The decline in $CO_{2(aq)}$ causes the reaction no (5) to show a tendency to the left side thus increases the pH of the solution. The increase in pH causes the the brine to become oversaturated in respect to calcite and thus precipitation of calcite occurs. To examine the reason of the decline in the saturation of calcite with increasing pH, let us take a look at the following reaction of calcite formation:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) \qquad (6)$$

When we add a strong acid like HCl(l) to $CaCO_3$(s) , the following reaction occurs:

$$2H^+(aq) + CO_3^{-2}(aq) \rightarrow H_2CO_3(aq) \qquad (7)$$

Then we start to see bubbles of gas as the following reaction occurs:

$$H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g) \qquad (8)$$

As $CO_3^{2-}$ ions react with the acid, reaction no (6) goes to the left and the solid $CaCO_3$ dissolves.

To sum up; the most important parameter effecting scaling is pH. A high pH will lead to increase in the concentration of carbonate ions, therefore will induce scaling. Dissolved $CO_2$ causes carbonic acid to form and thus lowers the pH, preventing scaling of $CaCO_3$. Removal of $CO_2$ however, causes the pH of the brine to rise and therefore induces the $CO_3$ to form a compound with $Ca^+$ and precipitate.

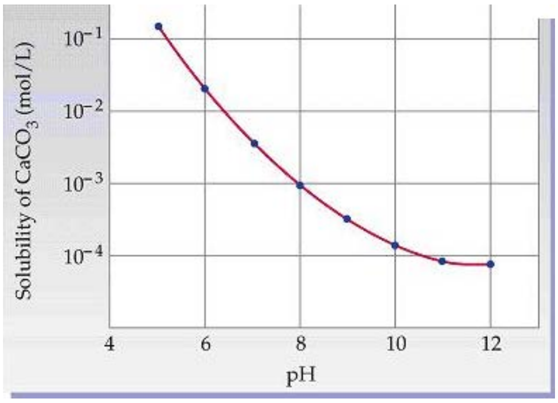

**Figure 3. Effect of pH on $CaCO_3$ Solubility**

$CaCO_3$ saturation increases with increasing $CO_2$(g) partial pressure and decreases with increasing temperature. Both parameters can be controlled up to some extent and give us important clues about calcium carbonate scaling:

- Scaling starts with boiling.
- Scaling will not form as long as the flow pressure is above the partial pressure of $CO_2$.
- Calcite solubility is inversely proportional with temperature, thus more calcite will be dissolved at low temperatures.

We may come up with some conclusions in parallel with the items above:

- We do not expect calcite scaling in locations where temperature drops.
- Calcite scaling will not occur as long as the boiling of the brine is prevented.

The latter is not always possible to practice, because keeping the system pressure above the partial $CO_2$ pressure will inhibit or decrease production in most wells.

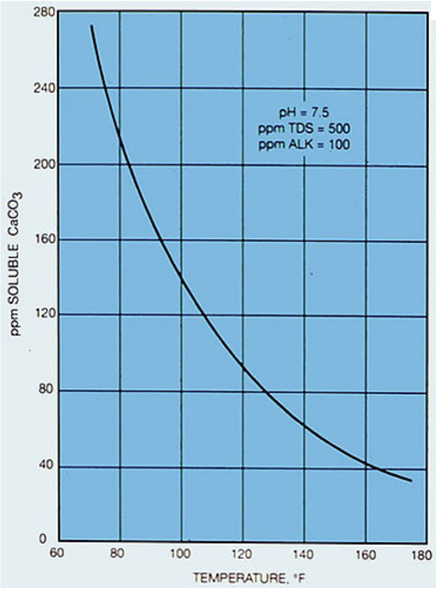

**Figure 4. Solubility of $CaCO_3$ with Temperature**

One common method to keep the flow pressure above the partial pressure of $CO_2$ is to use downhole pumps. A downhole pump installed below the boiling point will increase the pressure of the fluid and prevent it from boiling. Yet, this method is expensive since a special pump resistant to temperatures up to 200 ˚C is needed. The installation and maintanence requires top notch engineering skills and also the operation of the pump consumes a lot of energy.

## 2.2 Silica Scaling

Silica scaling is probably the most troublesome scaling encountered in geothermal systems due to its stiff crystalline structure.

When silica saturated geothermal brine evaporates, it becomes oversaturated with respect to silica and scaling starts to occur. Silica scaling is mainly dependant on pH, temperature and silica concentration.

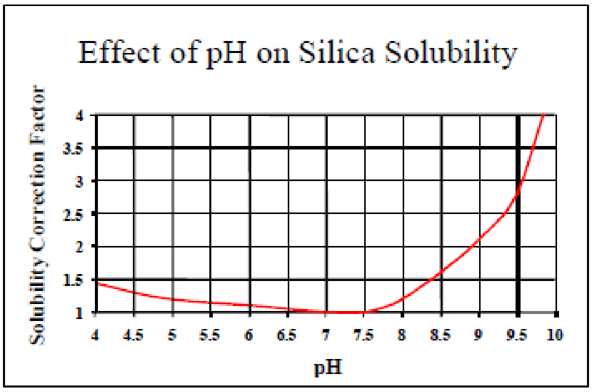

**Figure 4.Effect of pH on Silica Solubility**

Silica concentration in geothermal brine is usually below 700 ppm, because silica solubility reaches maximum(770 ppm) at 340˚C. Typically a concentration between 100-300 ppm is expected in geothermal brine.

Most common forms of silica precipitation is quartz, cristobalite and amorphous silica. When geothermal brine temperature drops, silica becomes oversaturated(see figure 5), usually as amorphous silica, and precipitates. This process causes major problems in reinjection wells and pipelines.

Removal of silica precipitation is a messy and time consuming process. It can be accomplished by mechanical and chemical treatments. Mechanical treatment alone is usually not enough and must be conducted in parallel with chemical treatments such as acidizing with HF(hydrofluoric), $NH_4HF_2$(ammonium hydrogen bifluoride) and HCl(hydrochloric).

Silica scaling can be prevented by lowering the pH below 5 by adding HCl or increasing pH rapidly by injecting NaOH. Silica can also be deposited as calcium silicate by addition of limestone. Another option is to keep the brine in pools until silica precipitates and then do the reinjection. But probably the most efficient way is to never let brine temperature drop below the point of silica saturation.

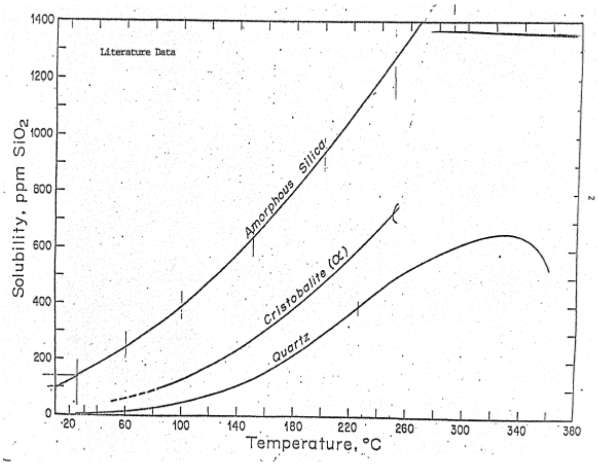

**Figure 5. Silica Solubility with Temperature**

### 2.3 Saturation Indices

Saturation index is an indicator of the solubility of water in respect to a mineral. It may show whether a water will tend to dissolve or precipitate a particular mineral. Its value is negative when the mineral may be dissolved, positive when it may be precipitated, and zero when the water and mineral are at chemical equilibrium. The saturation index(SI) is calculated by comparing the chemical activities of the dissolved ions of the mineral(ion activity product, IAP) with their solubility product($K_{sp}$);

$$SI = \log\left(\frac{IAP}{K_{sp}}\right) \tag{9}$$

The saturation index may be calculated by various computer codes such as WATCH, WATSPECT, PHREEQC etc. Saturation indices of production wells HB5, HB7 and HB8 have been calculated for aragonite, calcite and quartz using the computer code PHREEQC as given in the table below. The calculations were made for the sampling temperature of 98˚C degrees.

| | Aragonite | Calcite | Quartz | Amorphous Silica |
|---|---|---|---|---|
| HB5 | 1.0683 | 1.1699 | 0.2536 | -0.6337 |
| HB7 | 0.9161 | 1.0177 | 0.6027 | -0.2846 |
| HB8 | 0.5632 | 0.6648 | 0.571 | -0.3163 |

**Table 1. SI Values for Aragonite, Calcite and Quartz**

As can be seen in table 1 above, aragonite, calcite and quartz are all candidates for scaling minerals, yet the calculated SI values are not realistic because they are calculated from the sampling conditions of the brine. While sampling the brine it is exposed to atmospheric pressure and eventually flashes. This flashing causes the $CO_2$ to escape and pH to rise, yet the brine condition in the reservoir or the system is lost. Even these SI calculations are good indications of predicting scaling amount, as HB5 really is the most problematic well as can be seen in Table 1 when it comes to $CaCO_3$ precipitation, which we think is due to its high $Ca^{++}$ content. There is a cold water zone above the hot reservoir in HB5 and we think this cold zone is the reason for the high Ca++ content of this well since temperature is inversely proportional with $CaCO_3$ solubility.

What catches the eye in Table 1 is the amorphous silica solubility indexes being “minus” which means that silica is dissolving rather than precipitating. The reason this is happening is the temperature. As you can see in Figure 5, at 98˚C degrees of temperature, solubility of silica is close to 400 ppm. Yet, the silica concentration of the wells are much less than 400 ppm. A brief composition of the 3 brine samples are as follows;

| | HB5 | HB7 | HB8 |
|---|---|---|---|
| Mg | 26.9 ppm | 7.2 ppm | 3.3 ppm |
| $Ca^{++}$ | 20.9 ppm | 6.3 ppm | 3.1 ppm |
| $Na^{+}$ | 1581.0 ppm | 1352.0 ppm | 1535.0 ppm |
| $Cl^{-}$ | 1477.5 ppm | 1436.0 ppm | 1659.1 ppm |
| K | 79.9 ppm | 126.4 ppm | 104.1 ppm |
| $SiO_2$ | 84.3 ppm | 253.3 ppm | 221.4 ppm |
| B | 51.7ppm | 62.84 ppm | 63 ppm |

**Table 2. Concentration of the Production Wells**

Let us take a look at the table below which shows the amorphous silica saturation indices of the 3 samples for different temperatures;

| | HB5 | HB7 | HB8 |
|---|---|---|---|
| 98˚C | -0.6337 | -0.2846 | -0.3163 |
| 80˚C | -0.5278 | -0.1513 | -0.1880 |
| 70˚C | -0.4645 | -0.0728 | -0.1124 |
| 60˚C | -0.3979 | 0.0086 | -0.0339 |
| 50˚C | -0.3276 | 0.0927 | 0.0475 |

**Table 3. SI values of amorphous $SiO_2$ for different temperatures**

As can be seen in the table above, alarm bells start to ring at 60˚C degrees for HB7 as it is the well with the highest silica concentration.

## 3. PREVENTION OF SCALING

Most common effective method for controlling scaling is the use of chemicals. Chemicals, usually referred to as inhibitors, are injected through a capillary tube below the boiling point of the well. These inhibitors prevent the formation of mineral compounds and salts by encircling and holding certain cations.

### 3.1 Inhibitors

Geothermal inhibitors mainly consists of a few raw materials which may be classified basically as three types;

- Phosphonic acid inhibitors.
- Inhibitors manufactured by phosphonic acid salts such as Na and K.
- Polymer inhibitors

Phosphonic acid inhibitors are probably the most effective inhibitors due to their high concentration of active agents. They show great performance even at very low dosage rates. But their acidity(pH<2) is their drawback as they cause serious corrosion especially in high temperature wells. Taking into consideration that pH decreases 0.5 units every 60˚C increase in temperature, we expect the pH of the diluted solution to be in between 0.5-1.0. It is this catalyst effect of temperature that increases the corrosive effect of acidic inhibitors and brings forth a necessity of caution while working with them.

Using the Na and K based alkalies of phosphonic acids, phosphonic acids' pH may be neutralised. However, the active agent concentration of these raw materials will decline about %50 compared to their acidic forms, thus a higher dosage rate will be required to obtain the same performance.

Polymer inhibitors are usually used in very high temperatures and pressures due to their high stability at such conditions.

### 3.2 Inhibitor Injection System

A custom made injection system is manufactured consisting of an inhibitor tank, 1/2" pvc piping with two water filters, 2 diaphragm pumps and a drum coiled with 5/16" stainless steel tubing and an hydrolic brake system all on the same frame.

### 3.2.1 The Tubing

The tubings used for the injection of chemicals are 5/16", type 316L, bright annealed and their inner diameter is 4,8 mm.

### 3.2.2 The Pumps

Pumps are hydraulic diaphragm pumps with a maximum capacity of 19 lt/h each. Two pumps are connected parallel and one is used as redundant.

A manometer is mounted at the discharge line of the pump and is a very crucial equipment as it shows if there is a blockage in the tubing or not.

### 3.2.3 The Filters

The filters are basic water filters with 50 micron mesh. Their role is to hold the particles which may get mixed up during the filling process and may damage the pump or clog the tubing.

### 3.2.4 Graduated Cylinder

The graduated cylinder is mounted at the suction line of the pumps. It is used for measuring the flow rate of the inhibitor and by this way calculating the dose rate in ppm's.

The calculation procedure of the dose rate is as follows;

First the graduated cylinder is filled up to 0,5 liters and the time it takes to pump the 0,5 liters is recorded. Let's assume 0,5 liters is pumped in 2 minutes. This gives us a flow rate of 15 L/h. Since we are injecting a water-inhibitor mixture prepared with a fixed concentration of, let's say 1/15; the flow rate of the inhibitor alone as mass per hour is calculated as:

15 L/h x 1/15 x 1,413 kg/L = 1.413 kg/h

where, 1,413 kg/L is the density of the inhibitor.

If we assume that the flow rate of the well is 400 t/h, the dose rate is calculated as follows:

1,413 kg/h / 400.000 kg/h = 0,0000035 which we can refer to as 3,5 ppm.

### 3.2.5 Reducer

A reducer is used to rotate the drum via a chain transfer. A reducer is basically a worm-gearing device to reduce the rotational speed being transmitted from the motor shaft to the drum.

### 3.3 Selection of the Inhibitor

Dozens of inhibitors were developed during the recent years in parallel with the growth of the geothermal energy sector. The inhibitor must be chosen wisely for it may prevent scaling but may cause corrosion or blockage in the tubing.

Tests for the selection of the inhibitor were conducted in Irem power plant for three candidates of different brands.

To explain the test process briefly; each well is injected a high dosage at the beginning and the dose rate is slowly decreased while checking the control points. The chemical which can work with the lowest dose rate wins. This is the standart procedure for conducting inhibitor tests in geothermal fields.

Two control points were checked during the tests in Irem Power Plant; the total hardness measurement and the coupons.

### 3.3.1 Total $CaCO_3$ Hardness Measurement

This measurement is perhaps the most practical and the most dependable.

Hardness of water is a measure of the total concentration of the calcium and magnesium ions expressed as calcium carbonate.

In this procedure, a water is buffered to pH 10.1 and indicator is then added to the buffered sample. The indicator, when added to a solution containing Ca and Mg ions, turns red. EDTA, the titrant, complexes with Mg and Ca cations, removing them from association with the indicator. When all the Mg and Ca are complexed with EDTA, the indicator will turn blue. The amount of EDTA consumed x 10 gives us the total hardness in mg/L.

The logic behind this method is as follows; if a decrease in hardness is detected, then it means some of the $Ca^{++}$ cations are lost somewhere along the path and the most common way they are lost is by precipitating as $CaCO_3$.

Eventually, the winning chemical is the one that does not cause a drop in the total hardness with the minimum dose rate.

### 3.3.2 The Coupons

Coupons are 1-1,5 meter rods that are mounted into the pipe to determine if there is a precipitation occurring in the pipeline or not. They are mounted with bolted joints so they are removable. However coupons must be approached with maximum caution as they are mounted in pipelines with pressures of 10-20 bars and any wear on the rabbets or threads may cause them to thrust up like a spear.

Coupons can be tricky when trying to determine if $CaCO_3$ is precipitating or not, due to the fact that precipitation may occur in specific points in pipelines, like pump suctions, elbows or elevations where pressure drops occur. Since it is not feasible and practical to mount coupons on all these points, seeing a clean coupon with no precipitation does not always mean that the brine is not precipitating.

Eventually, coupons can be used as back up controls if hardness measurement fails to shed light on the situation.

### 3.4 Test Results

Below is the lowest working dose rates of inhibitors A, B and C during the tests.

| | A | B | C |
|---|---|---|---|
| HB5 | 3 PPM | 3,5 PPM | 4,5 PPM |
| HB7 | 2,5 PPM | 3,5 PPM | 4 PPM |
| HB8 | 2,5 PPM | 3,5 PPM | 4 PPM |

**Table 4. Lowest Working Dose Rates of Inhibitors**

The performance of inhibitor A was impressive and eventually it was the winning candidate and an agreement was made.

## 4. OPERATION OF THE PLANT

Various control parameters must be taken into consideration during the operation of a geothermal power plant which are ranked below.

### 4.1 Manometer of the Inhibitor Injection System

As stated before, a manometer is mounted at the discharge line of the injection pumps. This manometer is crucial since it may indicate a blockage in the tubing, as it did in Irem Power Plant in the third week of its operation.

The pressure reading in the manometer, although dependant on the well head pressure, will not usually exceed 10-15 bars as the inhibitor's hydrostatic pressure will almost equalize the back pressure of the well. But something unexpected happened during the operation of Irem and the pressure reading in HB8 increased up to 40 bars. Other wells also started to show high pressure readings in short notice. The increase in the back pressure readings did not cease, on the contrary they showed a rapid increase and reached a maximum of 100 bars in a few hours, thus the plant went to emergency shutdown.

As a result, we may come to the conclusion that one of the most important parameters in selecting the appropriate inhibitor is its stability against temperature.

After this incident, the contract with the inhibitor company was terminated and a new agreement was made with another company, however two weeks of financial damage was irrecoverable.

### 4.2 Consumption time

While it is inevitable for a poor quality inhibitor to be cooked in the tubing as explained above, we may however lower the chance by controlling the consumption time.

Consumption time is the time inhibitor spends in the tubing until it is injected into the well. The longer it stays in the tubing, the more chance it has to be cooked and clog the tubing. If we know the inner diameter and the length of the tubing we may calculate its volume. When we divide the volume by the flow rate of the inhibitor the result will be the time it spends in the tubing. No more than two hours is recommended but there is no certain estimation for it.

### 4.3 System Pressure

No matter how successful the inhibitor is, pressure drops below the saturation pressure of the brine should be avoided.

Irem power plant was operated just at the limit of the saturation pressure for the first few months. Pressure drops below the saturation pressure were inevitable. Some were caused by trips and some were caused by operation mistakes. After some time the vaporizer pressure difference between the inlet and outlet started to increase up to 3 bars while it should be at maximum 0,1 bar. Eventually a cleaning was required and the plant shut down for a week.

As a result, it will be wise to keep the pressure at least 2 bars above the saturation pressure to play it safe and maintain a constant pressure in the system.

### 4.4 Sampling Points

The more sampling points there are, the more precisely we can find the location of scaling. For example, a sampling point before and after the accumulator will indicate if there is scaling in the accumulator or not.

Let's assume that the total hardness measurement before and after the accumulator is 90 and 80 ppm respectively. This will show us that there is scaling occurring in the accumulator, as the only explanation for the disappearance of 10 ppm $Ca^{++}$ is its precipitation as $CaCO_3$.

### 4.5 Optimum Dosage

Optimum dosage is crucial for a healthy plant operation. More dosage then needed will not help prevent scaling more efficiently, rather it will lead to precipitation of by- products of the inhibitor such as calcium phosphate.

Calcium phosphate looks just like calcite. Even an experienced eye would not know the difference. The first measure to take here is to dip the deposit in hydro chloric acid to see if it will react or not. This measure should be applied to all the encountered deposits, as by time operational blindness may emerge and you may end up injecting more and more, supposing the deposit at hand is calcium carbonate.

## 5. CONCLUSION

Scaling and corrosion is a big problem in geothermal power plants. It is inevitable to face scaling problems in the start-up period, but a close disciplined inspection and having a theoretical knowledge of the cause of scaling will soon get the plant back on track.

The most important factor needed for a smooth operation is probably the selection of the inhibitor. Nowadays everyone out there is making chemical inhibitors. It is not wise to take risks by signing with companies that have no experience in the field or whatsoever as they may cost you irrecoverable financial damages.

Irem Power Plant is running smoothly without any scaling problems now. Controls are never skipped and measurements are taken almost everyday, as a disciplined observation of the field is the key to a successful operation.

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