



# **Best practice guide for the operation of geothermal plants to avoid corrosion**

## **Task 5.5 GEOTHERM project**

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## 1 Dansk resumé

Denne drejebog sammenfatter erfaringerne fra GEOTHERM projektet, som fokuserer på at fjerne barrierer for udnyttelsen af geotermisk energi i Danmark. Tilstopning af injektionsbrønde er her en generel udfordring for geotermisk energi, og det ses ikke kun i danske anlæg. Drejebogen fokuserer på tiltag der kan minimere korrosion i anlægget og dermed nedsætte partikelafgivelse i form af rust. Sådanne partikler kan over tid føre til trykopbygning i brøndene, og det er kun muligt at fjerne dem igen ved kostbare brøndoperationer (såsom udsyring). Bekæmpelsen af korrosion har desuden til formål at forlænge anlæggets levetid samt at sikre stabil drift og forhindre utilsigtede stop. Drejebogen gennemgår de typiske anlægsdesign og materialer for danske anlæg, og introducerer herefter mulige korrosionsformer, som kan forekomme i det saltholdige geotermiske vand (brine). Korrosion af stålrør i brøndene og overfladeanlæg kan opstå som følge af iltindtrængen, gasser i reservoiret (især CO<sub>2</sub>) eller ædle metalioner i vandet. Specielt kan indtrængen af ilt føre til stor partikelafgivelse, hvilket underbygges af beregningseksempler. Iltindtrængen bør hele tiden overvåges og forebygges i anlægget. Korrosion som forårsages af reservoirets kemi forebygges oftest ved injektion af korrosionsinhibitor i produktionsbrønden. Her er det ligeledes nødvendigt at overvåge virkningen konstant. Korrosionsovervågning er derfor en vigtig del af denne drejebog, og alle teknikker fra simple korrosionskupper til avanceret on-line måling gennemgås og vurderes. Korrosionsovervågning skal betragtes som en ufravigelig del af den overordnede drifts- og vedligeholdelsesplan for det geotermiske anlæg på linje med procedurer for regelmæssigt tilsyn af udstyr, analyse af vandprøver, evaluering af procesdata etc.

## 2 Executive summary

This best practice is the result of Work Package 5 (WP5) in the GEOTHERM project with the objective of addressing the problems of injectivity in the Danish geothermal plants. Blockage of injection wells is a general challenge for geothermal energy, and it is not only seen in Danish plants. The best practice focuses on efforts that can minimize corrosion in the plant and thus reduce particle release in the form of rust. Such particles will, over time, lead to pressure build-up in the wells, and it is only possible to remove the clogging again by costly well operations (such as acid jobs). The purpose of combating corrosion is also to extend the life of the plant and to ensure stable operation with no unscheduled stops. The best practice reviews the typical plant designs and materials for Danish plants, and then introduces possible corrosion types that can occur in the saline geothermal water (brine). Corrosion of steel tubing in the wells and surface plant can occur as a result of oxygen ingress, gases in the reservoir (especially CO<sub>2</sub>) or metal ions in the water. In particular, ingress of oxygen can lead to considerable particle release, which is demonstrated by calculations. Oxygen ingress must be constantly monitored and prevented in the plant. Corrosion caused by the chemistry of the reservoir is usually prevented by injection of corrosion inhibitor into the production well. Here it is also necessary to constantly monitor the effect. Thus, corrosion monitoring is an important part of this best practice. All techniques from simple corrosion coupons to advanced on-line measurement are reviewed and evaluated. Corrosion monitoring should be regarded as a mandatory part of the overall operation and maintenance plan for the geothermal plant alongside with procedures for regular equipment inspection, water sampling and review of process performance etc.

### 3 Foreword

The GEOTHERM project in 2017-2019 is co-funded by Innovation Fund Denmark. The full title of the project is: Geothermal energy from sedimentary reservoirs – Removing obstacles for large scale utilization. Innovation Fund Denmark: project 6154-00011B. The best practice finalizes the reporting of Milestone M5.5a in Work Package 5 that focussed on aggressive geothermal brines, corrosion, scaling and microbiology. Work Package 5 included the following partners: GEUS, Geop A/S, Sønderborg Varme A/S, Høfor A/S, Thisted Varmeforsyning Amba and FORCE Technology. Additionally, international partners have contributed to the project, i.e. BRGM, GFZ Potsdam and Lunds Universitet. The best practice was edited by Troels Mathiesen and Jakob Mølholm at FORCE Technology.



## 4 Introduction

The best-practice covers the aspects of aggressive brines in geothermal energy plants with particular focus on corrosion of the metallic equipment that may contribute to plugging of the injection wells, thereby reducing the injectivity. Reduced injectivity is a major challenge in geothermal energy and not only in Danish plants. Apart from corrosion, other mechanisms are known to affect injectivity such as scaling due to instability of the geothermal water, microbiologic growth that may form insoluble by-products, incorrect design of well and gravel pack or gradual changes in the formation when water is reinjected. It is the scope of this best-practice to deal specifically with mechanisms involving corrosion, i.e. the interactions between brine and equipment that possibly could cause particle release but also may reduce the lifetime of the plant. At the same time corrosion increases the need for maintenance, well work-overs and causes unscheduled downtime of the plants operation.

The typical layout of a geothermal plant is shown in Figure 1. This type of plant is also known as a doublet having two wells, a producer (1) and an injector (8). Apart from that, 9 other elements describe the design and operation of the plant.

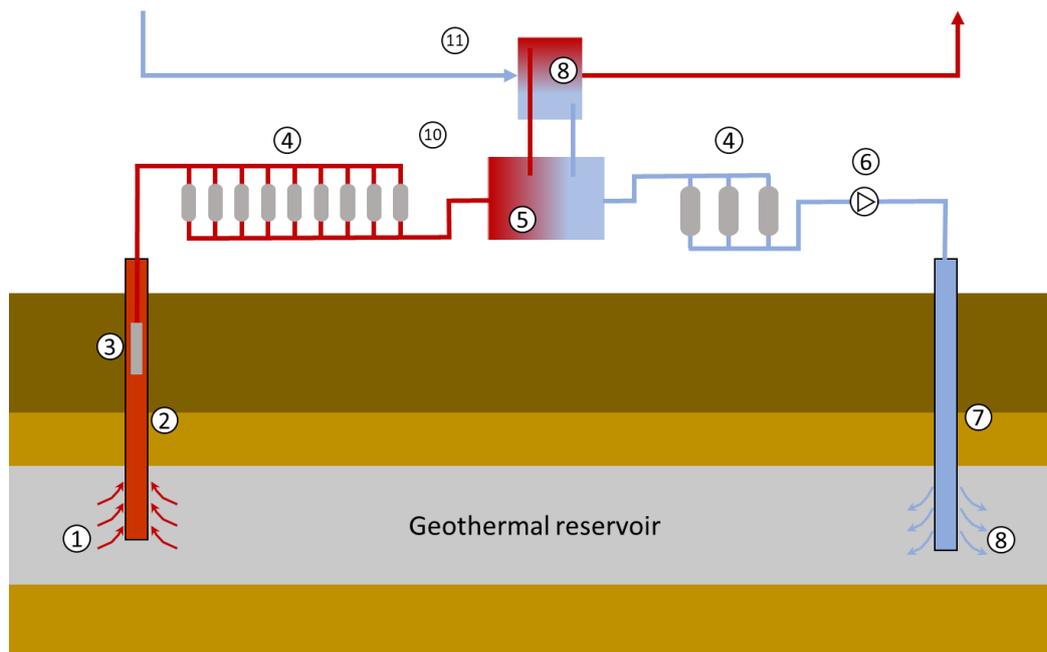
The three existing Danish facilities are comparable with only minor differences in formation type, plant design and operation. While the oldest plant in Thisted (THI) has had only minor problems with reduced injectivity over time, Margretheholm (MAH) and Sønderborg (SFJV) are both experiencing considerably reduced injectivity. Several reports review the problems, refs 1-2.

The Danish plants use non-coated steel tubing for the wells (except for the most recent well in Thisted). An electrical submersible pump (3) in the production well feeds the surface installation with warm brine from the sandstone reservoir. The brine is filtered in bag filters in stainless steel or steel canisters (4) before reaching the titanium plate heat exchangers (MAH and SFJV) or the absorption heat pump (THI). Compact cartridge filters (4) remove particles before the brine finally is reinjected into the formation again, sometimes using an injection pump (6).

The brine solution is potentially very corrosive due to the high salt concentration (16-22 %, Na-Ca-Cl). Strict precautions such as nitrogen or argon blanketing during standstill periods are applied to avoid ingress of air/oxygen, thereby removing the driving force for corrosion. As discussed later, other substances may also affect corrosion such as dissolved metal ions ( $Pb^{2+}$ ) or dissolved  $CO_2$  gas. The use of dissimilar metals (carbon steel, stainless steel and titanium) may in addition present a risk of galvanic corrosion.

During normal operation 100-300 m<sup>3</sup> warm brine (50-75 °C) is circulated through the plant every hour. The known causes for unscheduled stops or interruptions include injection well plugging, filter replacement, wear in pump due to sand production and heat pump failure (LiBr brine corrosion). This best practice focus on the conditions in the main circuit of geothermal brine, being the most important one to secure the injection well and provide uninterrupted service for +30 years.

Having only three plants in Denmark, geothermal energy is still a young industry today. Thus, there are no exact guidelines yet about planning, design and operation. However, valuable experiences have been obtained from the project's international partners in Germany, France and Sweden where geothermal energy is more frequent. As an example, the geothermal plants in Paris must comply with national guidelines to maintain their insurance policy and financial support, ref 3. The plants in Paris produce from carbonated reservoirs so the conditions are not the same as those found in the Danish sandstone reservoirs.



No	Description	Materials in contact with brine
1	Producer, lower completion	Carbon steel, stainless steel EN 1.4401
2	Producer (well bore)	Carbon steel, composite (GRE)
3	Production Electrical Submersible Pump (pESP)	Abrasion and corrosion resistant alloys (CRAs)
4	Filtration	Coated steel, stainless-steel canisters
5	Heat exchanger	Titanium plates, 17Cr stainless steel tubing
6	Injection Pump (iP)	Corrosion resistant alloys (CRAs)
7	Injector (well bore)	Carbon steel, composite
8	Injector, Lower completion	Carbon steel, stainless steel EN 1.4401
9	Heat Pump	Carbon steel, 17Cr stainless steel tubing
10	Auxiliary systems	
11	District heating loop (distribution)	

Figure 1. Schematic of geothermal plant including 11 elements showing typical selection of materials used in Denmark.

Valuable experience has also been gained from literature and guidelines about water injection systems in oil and gas production, ref 4. Such systems are comparable with geothermal injection system as to materials,

corrosion, operation and requirements for monitoring. The injected water for oil production is often a mixture of seawater and produced water from the reservoir. Seawater contains a wide range of microbiologic organisms and nutrients, while the geothermal brine usually is free from such constituents. If not present in the geothermal reservoir, contamination with bacteria may, however, still occur during shut-downs, maintenance or well workovers in the geothermal facility. In the oil and gas industry it is also well known that bacteria in the injected seawater may cause souring ( $H_2S$  production) of the reservoir leading to complications in the producing wells. Such scenarios are yet not known for geothermal energy, but efforts must still be made to control bacteria.

## **5 The need for corrosion control**

It is important to control corrosion damage in the carbon steel tubing pipework for several reasons. Perhaps most obviously is the need to reduce the amount of particles in the system, because it can cause blockage of the injection well or result in formation damage. It is known from seawater injection wells in oil and gas industry that corrosion products (e.g. iron oxide and iron sulphide) and bacterial biomass have caused considerable damage, even in formations with high permeability, ref 4.

Great efforts are already applied in the surface plant design to reduce such particles by filtering, but the injection line and well includes several kilometres of steel tubing where the problems might reoccur. Since a geothermal plant is intended to work well for at least 30 years, control of corrosion shall be taken very seriously from day one.

Corrosion damage also involves a risk for the projected lifetime and integrity of the equipment. Since the majority of the installations is subsurface, maintenance and repair are complicated and very costly, requiring specialized contractors. The installations in the surface plant are easier to access, but any interruption in service is still undesirable due to the costs of loss in production, repair as well as laborious operations for shutdown and resuming service.

Other concerns of corrosion include reduced efficiency of the heat exchangers, if corrosion leads to scaling and loss in heat transfer.

Finally, and equally important is the risk of penetrating corrosion in well tubings, since this could potentially contaminate upper reservoirs, such as ground water reservoirs with brine or chemicals (if corrosion inhibitor is used).

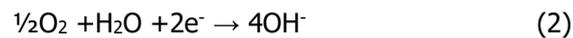
## 6 Corrosion types in geothermal brine

The geothermal brine, having a salinity of 16-22 %, makes it potentially very corrosive to most metals. For comparison, the salinity of seawater is just 3.5 %.

The salts, mainly Na, Ca and Cl, are not the main driving force for corrosion, but they provide the possibility of the long-range galvanic elements due to the high electrical conductivity of the geothermal brine (approx. 150 mS/cm). This is obvious from the character of aqueous corrosion of iron (or steel), being an electro-chemical reaction that involves release of electrons according to equation (1):



Corrosion only occurs if this reaction (anode) is balanced by an electron consuming reaction (cathode), such as oxygen reduction (2) or hydrogen reduction (3):



Both reactions are known in geothermal brines. However, corrosion due to oxygen would usually imply unintended ingress of oxygen to the closed system, because the geothermal brine is completely free from oxygen in the reservoir. Corrosion due to acid ( $\text{H}^+$ ) may arise from dissolved gasses in the brine such as  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , both being weak acids. Acid ( $\text{H}^+$ ) may also come from the natural dissociation of water (anoxic corrosion), but usually the amount is so small in pH-neutral brine that this type of corrosion is negligible.

Deposition of dissolved metal ions, such as lead (4), is also known to cause corrosion in certain brine types:



Carbon steel usually accounts for the majority of the installations in well tubing and pipework in the surface plant. The dissolved iron quickly forms insoluble corrosion products such as magnetite ( $\text{Fe}_3\text{O}_4$ ) with the possibility of plugging the injection well.

Corrosion resistant alloys (CRA) are used for various equipment and instrumentation. E.g. titanium is used for plate heat exchangers and stainless steel type EN 1.4401 is used for instrument tubing and canisters for filters. As discussed below, the CRAs are only susceptible to oxygen ingress whereas carbon steel is susceptible to all corrosion mechanisms shown in Figure 2.

### Uniform corrosion

Uniform corrosion is only possible for carbon steel in the brine solution, Figure 2a. Several cathode reactions may facilitate this reaction including oxygen reduction and hydrogen reduction. High flow conditions or elevated temperature conditions may favour rapid corrosion in some areas while other areas may be partly covered by rust products (iron oxide), slowing down the process here.

### Pitting and localised corrosion

Pitting corrosion is mainly a problem for CRAs that are protected by a passive oxide layer. Even trace levels of oxygen may cause pitting, especially for low alloy grades like 17Cr or EN 1.4401 stainless steel. Corrosion becomes very localised in the pit because the majority of the surface remains passive, at the same time facilitating the cathode reaction. Moreover, the metal-rich and low-pH solution formed in the pit makes the corrosion self-catalytic, Figure 2b.

If stainless steel components are coupled to carbon steel, no corrosion will take place because the less noble carbon steel provides cathodic protection at the cost of faster corrosion of this steel. Thus, the risk of severe pitting is only relevant if larger sections of stainless steel (pipework, heat exchangers or pumps) are installed. This is also the reason why highly resistant titanium is used in the plate heat exchangers

Pitting corrosion and localised corrosion may also occur on carbon steel, if the steel is partly covered by electrically conductive scales such as iron sulphide.

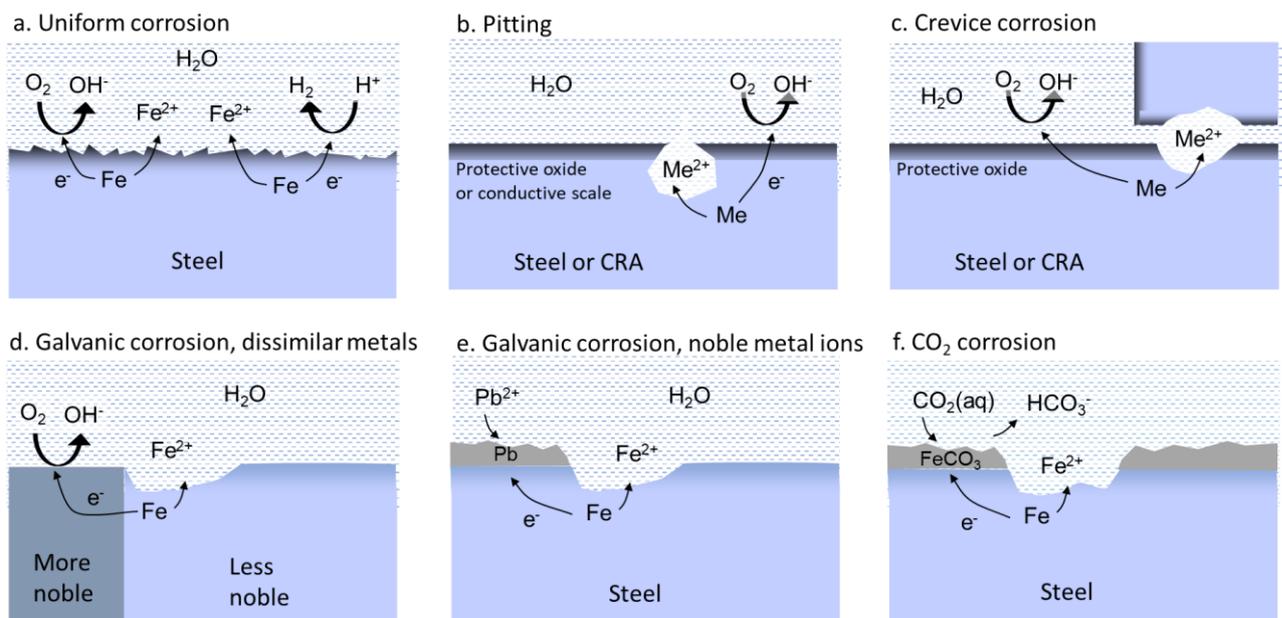


Figure 2. Simplified depiction of corrosion types that can occur in geothermal brine.

### **Crevice corrosion**

Crevice corrosion has many similarities with pitting, because it is promoted by an oxygen concentration cell between passive and active areas, and by the trapping of an aggressive solution inside the crevice, Figure 2c. It is mainly a problem for low alloy CRAs, provided oxygen is present in the brine. Common areas to find crevice corrosion include flange joints, threaded joints or small cavities filled with brine.

### **Galvanic corrosion – dissimilar metals**

Galvanic corrosion occurs when two dissimilar metals are in contact, and at the same time having a liquid connection between the two metals. In geothermal systems, oxygen reduction is the only likely cathode reaction for driving this process. Thus, galvanic corrosion is only considered, if oxygen ingress happens.

The principle of galvanic corrosion is comparable with a battery cell. If the metals are more than 0.1-0.2 V apart in the galvanic series, there is a considerable risk of corrosion of the less noble metal on behalf of the more noble metal, Figure 2d. Stainless steel is ~0.6 V more noble than carbon steel in geothermal brine, thereby presenting a risk of galvanic corrosion. If the surface area of the noble metal is much larger than that of the less noble metal, the unfavourable area ratio will lead to extremely rapid corrosion. Due to the high electrical conductivity of the brine, the galvanic element includes surfaces over long distances, making this mechanism particularly dangerous in geothermal plants.

For the same reasons, care must be taken when defining the welding procedure for steel tubing in geothermal plants to avoid galvanic differences between the weld metal and the parent pipe metal. Usually, weld metal is added small amounts of nickel and chromium to optimise the mechanical properties. The addition of such noble elements would typically imply higher corrosion resistance of the weld than the parent metal, but in some situations the effect is opposite leading to a phenomenon known as Preferential Weld Corrosion (PWC). It is always advised to make a prequalification corrosion testing of the welding procedure to avoid this problem before building the plant.

### **Galvanic corrosion – noble metal ions**

A special form of galvanic corrosion, involving noble metal deposition, can happen in geothermal plants. In certain reservoir types, the brine contains dissolved metal ions, such as lead ( $Pb^{2+}$ ) in the Bunter reservoirs. And in Germany, dissolved copper ions ( $Cu^{2+}$ ) has caused galvanic corrosion in one plant.

Since lead is more noble than iron, the mechanism shown in Figure 2e can run. The tendency to lead deposition increases with increasing temperature and flow rate. Consequently, the production well and tubing are more vulnerable to this form of corrosion than the other sections.

### **CO<sub>2</sub> corrosion**

Carbon dioxide ( $CO_2$ ) is a weak acid when dissolved in water and thereby potentially corrosive to steel. The corrosion rate mainly depends on the partial pressure of  $CO_2$ , which can be high in pressurized systems like geothermal wells. By this  $CO_2$  becomes almost an inexhaustible source for the cathode reaction. There is

vast experience from oil and gas production, where CO<sub>2</sub> dissolved in the produced water is known to cause considerable corrosion. In the Danish geothermal wells only a small fraction of the gas from the production well is CO<sub>2</sub> (0.5-3.6%), whereas methane (CH<sub>4</sub>) and especially nitrogen (N<sub>2</sub>) make up the majority.

The mechanism of CO<sub>2</sub> corrosion is shown in Figure 2f. It involves formation of a partly protecting iron carbonate film, leading to localised corrosion of the steel. Usually, the corrosion rate increases with temperature up to a maximum at about 70-80°C. At higher temperature, the carbonate film becomes more stable leading to slower corrosion. Thus, the conditions in the production well (high temperature, high pressure) represent the greatest risk for CO<sub>2</sub> corrosion. Flow rate and buffer capacity of the brine are also decisive for the stability of the carbonate film and the resulting pH at the surface.

### **Other types of corrosion**

Other types of corrosion than the above could potentially occur and should be introduced briefly below.

Local high flowrates causing turbulence usually increases the corrosion rate of especially unalloyed steel by constantly removing the formed rust layer from the surface. This will happen if pipe bends are too sharp, and in extreme cases, erosion occurs too on the surface. Likewise, sudden pressure changes due to reduced sections in the pipework can lead to cavitation from the impact of collapsing gas bubbles on the surface. Supersaturation with dissolved gasses accelerate this mechanism further. However, usually the design of the plant is made to avoid such flow related degradation mechanisms by following well-established rules for hydrodynamic engineering.

Handling warm chloride solutions (>50°C) always presents a risk of stress corrosion cracking (SCC) for low-alloy stainless steel types such as EN 1.4401. This form of corrosion is particular dangerous because the combined effect of mechanical stress and chemical attack can lead to rapid cracking. Since oxygen is needed for the reaction to occur, the exterior surfaces of hot equipment are most vulnerable, provided there is a continuous spill (i.e. wetting) of chloride solution.

In line with this, the risk of corrosion under insulation (CUI) must also be considered for all types of equipment. Continuous wetting of the insulation from e.g. small leakages, rain etc. can cause severe corrosion of the hot metal surface due to the well-aerated conditions.

As mentioned previously, microbiologically induced corrosion (MIC) is well known in the oil and gas industry, but no incidents have yet been seen in in Danish geothermal plants.

### **Potential release of rust particles**

The amount of iron dissolved from either oxygen corrosion or deposition of metal ions can be calculated using stoichiometric calculations based on equations (1) to (4). Possible worst-case scenarios are given below to give an impression of the impact corrosion may cause on particle release. This is calculated as release

per year, but the Danish geothermal plants only operate half of the time during winter season. It is assumed that iron forms magnetite ( $\text{Fe}_3\text{O}_4$ ) which is the normal corrosion product in water with almost no oxygen.

### *Oxygen*

Ingress of oxygen could potentially dissolve 2 mg/l  $\text{O}_2$  in the high-saline brine at 25 °C, which is much lower than that of tap water (8-9 mg/l). At higher temperature the solubility is even lower. On-site measurements indicate that the dissolved oxygen (DO) level during excursions is about 0.2 mg/l. Assuming all oxygen is consumed by corrosion, the amount can  $\text{Fe}_3\text{O}_4$  can be calculated as:

Dissolved oxygen:	0.2 mg/l		
Flow rate:	200 m <sup>3</sup> /hr		
$\text{Fe}_3\text{O}_4$ formed:	190 g/hr =	1.7 t/yr =	0.34 m <sup>3</sup> /yr
Corrosion rate*:	0.2 mm/yr		

\*assuming uniform corrosion in 1.2 km 9 5/8" tubing

Presence of mill scale in the well tubings, as seen in one plant, may cause even higher release rates of the particles due to subsurface corrosion and flaking-off of the mill scale, ref 2.

### *Lead*

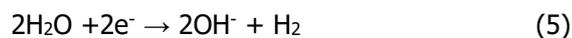
A similar calculation can be made for dissolved lead ions as the driving force for corrosion of steel:

$\text{Pb}^{2+}$ concentration:	0.4 mg/l		
Flow rate:	200 m <sup>3</sup> /hr		
$\text{Fe}_3\text{O}_4$ formed:	60 g/hr =	0.5 t/yr =	0.10 m <sup>3</sup> /yr
Corrosion rate*:	0.06 mm/yr		

\*assuming uniform corrosion in 1.2 km 9 5/8" tubing

### *Anoxic corrosion*

Corrosion due to the dissociation of water (5) without presence of oxygen should also be considered.



Corrosion rate measurements in the laboratory in deaerated brine (pH 7) predicts a corrosion rate of 25  $\mu\text{m}/\text{yr}$  in the temperature range from 25 to 70 °C on a fresh metallic surface. However, experience from completely deaerated location like ship wrecks in the seabed show an anoxic corrosion of steel in the range of 0.1-1  $\mu\text{m}/\text{yr}$ , ref 5. This is further supported by examination of a 30-year old pipe sample from a geothermal plant that had maintained ideal oxygen-free conditions in the brine. Based on this, the expected metal release from anoxic corrosion is roughly 200 times smaller than that of the 200 ppb  $\text{O}_2$  scenario, i.e.:

Corrosion rate:	0.001 mm/yr		
$\text{Fe}_3\text{O}_4$ formed*:	1 g/hr =	0.009 t/yr =	0.002 m <sup>3</sup> /yr

\*assuming uniform corrosion in 1.2 km 9 5/8" tubing

## 7 Corrosion control in geothermal brine

Corrosion in geothermal systems is usually caused by one of the mechanisms described in section 6, i.e. air ingress, noble metal ions or dissolved gases from the well, and to a smaller extent by anoxic corrosion or bacteria.

### *Deaeration*

It is always of outmost importance to keep the system deaerated, including start-up, operation, shutdown and standstill periods. Air entering the waterfilled system will lead to corrosion of carbon steel and possibly also low-alloy stainless steel. The calculations in section 6 indicate the release of iron that will form iron oxides or particles that could block the well. Moreover, ingress of oxygen could destabilise the brine and form other mineral precipitates.

As a basis, the brine from the reservoir is completely free from oxygen. Thus, possible ingress of air is related to operations in the plant (draining, repair, filter replacement etc.) or faulty and inadequate maintenance of equipment (leaking seals in pumps etc.). Efforts should constantly be applied to minimize the air entering the system from such sources.

During start-up, rock-the well operations are sometimes made to stimulate the injection well. This involves a pressure build-up with nitrogen followed by a rapid pressure-release. Pure nitrogen or other inert gasses like argon should be used for such operations. Compressed air should not be used for such well operations due to its high content of oxygen.

Typically, a technical grade nitrogen gas containing less than 100 ppm (v/v) oxygen is considered sufficiently pure. The heavier argon gas is recommended for blanketing above the water level in wells, if work at the well head leads to oxygen ingress here.

During normal operation, the risk of oxygen ingress is usually very small, especially if the system is pressurized. The injection pump represents a potential risk area for air-intake at the seal for the pump shaft due the suction forces. Usually, a special device prevents this from happening by applying a pressure of liquid and nitrogen on the outside of the seal. However, if not operated correctly, oxygen ingress could occur at this location while the pump is running. If the surface plant operates at slight underpressure, the risk of oxygen ingress is even higher and strict procedures should be established, e.g. continuous dissolved oxygen monitoring.

During shutdown for summer periods or repair, special precautions are also required to minimize air, entering the system. In most cases the system remains water-filled without circulation. Some equipment may be disconnected and opened, e.g. filters and heat exchangers. When refilling and reconnecting such equipment, air will inevitably enter the system. Blanketing and pressurizing with inert nitrogen gas are commonly used to displace air as a good practice.

Dosage of oxygen scavengers may be considered to limit the effect of oxygen during shut-down and stand-still depending on the amount of oxygen entering the system. Sodium sulfite, ammonium bisulfite or sodium bisulfite are frequently used in systems such as water injection systems, comparable with the geothermal circuit. Sometimes a catalyst is added in ppb concentration (e.g. cobalt) to speed up the reaction. However, before applying oxygen scavengers the potential risks and side-effects should be evaluated closely. As an example, sulfate and perhaps H<sub>2</sub>S formed by the reaction with sulfite could promote growth of sulfate reducing bacteria (SRB). Thus, it may be beneficial to add a biocide simultaneously together with the oxygen scavenger.

The operation of the geothermal plant should be planned to reduce the number of start/stop situations due to the possibility of air ingress, as mentioned above.

#### *Metal ions*

Metal ions in the brine, such as lead, can contribute considerably to the corrosion of carbon steel. Since such metal ions come from the reservoir, only a slow decrease in concentration can be expected throughout the entire lifetime of the plant. The decrease rate will depend on the exchange of brine between the interconnected formations.

Yet, there are no effective ways of removing such ions before the brine goes back into the injection well. Consequently, the only way to prevent corrosion is adding corrosion inhibitors. Corrosion inhibitors form an organic film on the metal surface, thereby obstructing the metal deposition and galvanic reactions from occurring. The efficiency depends on dosage concentration, flow, temperature and surface finish of the steel. It is advisable to conduct corrosion testing in a laboratory before deciding on the inhibitor type and dosage. Continuous corrosion monitoring in the operating plant is also recommended as discussed later.

Apart from chemical dosage, it may be considered to redesign critical details in the plant, where deposition of the metal ions is most likely. Turbulent flow is known to promote metal deposition, so it is advisable to avoid sharp pipe bends or sudden reductions in the pipe diameter. Likewise, elevated temperature promotes metal deposition of e.g. lead, so circulation with no cooling should be prevented in order to limit the problem to equipment upstream the heat exchangers.

#### *Dissolved gasses from the reservoir*

Dissolved CO<sub>2</sub> gas from the reservoir is a main concern for corrosion of carbon steel. The concentration may change from the production well to the surface, so correct sampling is crucial to determine a reliable value. A significant change in concentration is not expected over time.

Depending on the concentration, it may be considered to inject a corrosion inhibitor in the production well through a chemical injection line. This will reduce corrosion in the production well tubing to the surface and downstream equipment.

In the surface plant, where the pressure is relieved, CO<sub>2</sub> may come out as a separate gas phase. Removing the CO<sub>2</sub> gas from the brine in a de-gasser will be beneficial to avoid corrosion of downstream equipment. However, the resulting increase in pH could on the other hand affect the stability of the brine, leading to scale formation (e.g. calcite). Consequently, a geochemist should be consulted before installing a de-gasser.

Overall, dosage of corrosion inhibitor seems to be the most feasible method to prevent CO<sub>2</sub> corrosion. However, it is recommended to perform prequalification by corrosion testing in the laboratory as well as continuous corrosion monitoring in the operating plant to ensure high efficiency.

### *Bacteria*

Bacteria are mainly considered a potential problem during standstill periods. Water sampling and analysis can show whether there is a tendency to bacteria growth. Depending on this, it may be considered to treat the water with biocide. Oxidizing biocides such as chlorine (Cl<sub>2</sub>) or hypochlorite (NaOCl) are not applicable for the deaerated water system because they accelerate corrosion. Their effect on corrosion is the same as dissolved oxygen. Instead organic biocides to control anaerobic bacteria should be considered.

Care should be taken when selecting suitable biocides. Incorrect selection of biocide can cause compatibility issues with brine stability or other chemicals, particularly oxygen scavengers. Experienced chemical treatment companies with appropriate documented testing should be consulted to ensure full compatibility.

### **Staff, education and routines**

Operating the geothermal plant requires fully educated and dedicated staff, similar to running any other power plant. Any deviations in operation recorded by the SRO/SCADA system or should immediately be attended and evaluated for follow-up actions in accordance with predefined procedures. Even small excursions in operation could potentially cause increased corrosion or scaling, and in the end require costly work-over of the wells as a worst-case scenario. As discussed in the next section, on-line corrosion monitoring should preferably be part of this supervisory strategy for better corrosion control.

Observations from the equipment during operation, shutdown or maintenance should also be included in the daily procedures to control corrosion. Things to look for and keep a journal on include:

- Spill or leakages. Indicates corrosion from the inside. Furthermore, any leakage may cause even faster corrosion on the outside surface due to the contact with air.
- Characteristics of surfaces. Perform visual inspection of the inside surfaces whenever the equipment is opened. Look for anomalies such as pitting, preferential weld corrosion, scaling, metal deposition etc.
- Anode consumption in filters. Iron anodes are often used to protect the stainless steel canisters in filters. Record the consumption. A sudden increase indicates air-ingress in the system.
- Filter replacement intervals. The need for frequent filter replacement or increasing pressure drop over the filters indicates a problem with particle release, potentially rust.

## 8 Corrosion monitoring

Due to the potential impact on the injection well and equipment corrosion should ideally be monitored in the geothermal plant. Corrosion monitoring can in many cases prevent unscheduled stops or at least indicate when forthcoming interventions are needed. Based on the experiences obtained in the GEOTHERM project, various corrosion monitoring techniques are introduced below. The final configuration depends on the challenges met in the specific geothermal plant, i.e. whether it is oxygen ingress, CO<sub>2</sub> corrosion or dosage of corrosion inhibitor that needs to be controlled. Corrosion monitoring should be regarded as a mandatory part of the overall supervision and maintenance strategy for the geothermal plant alongside with procedures for regular inspection equipment, water sampling and review of process performance etc.

### Safety

Part of the geothermal plant operates at high pressure and high temperature, so safety is a key concern. Ideally, the corrosion probes should be installed a side-stream loop that can be disconnected without interfering operation of the geothermal plant, Figure 3. In this way, probes can be serviced without pressure in the lines.

Replaceable corrosion probes for direct installation (intrusive) in the pressurized pipework are available from several suppliers, and they are commonly used in oil and gas industry. However, we advise against this option due to the safety concerns and the extra training needed for using such probes and the special retrieval tools. If this path is chosen anyway, detailed information about safety and installation options can be found in ref 3.



Figure 3. Side-stream loop for corrosion monitoring in pressurized line downstream the injection pump.

### **Corrosion coupons**

The simplest way of corrosion monitoring is obtained by installing metal coupons in the same material as the pipework, Figure 4. Other configurations such as flush disc-probes are also available, giving a better resemblance of the flow conditions along the pipe wall. The pre-weighted coupons are exposed in pairs for several months and then retrieved for inspection, cleaning and weighing. By this, the accumulated corrosion rate for the exposure period is determined. Exposure should be at least one month to accommodate for the high initial corrosion rate of the metallic clean coupons.

The mounting direction of the coupons and flowrate in the sidestream loop should be considered closely to obtain flow conditions resembling the pipework. High flowrate causing turbulent conditions may give too high corrosion rates due to erosion and cavitation effects on the coupons.

The visual inspection of the coupon does at the same time provide essential information about corrosion type (uniform or pitting) and tendency to scaling. Scrape-off samples of the scale or products on surface can be analysed chemically to identify the mechanism for corrosion.

Additionally, corrosion coupons may be coupled in pairs of dissimilar metals to evaluate the risk of galvanic corrosion.

Corrosion coupons give a precise and direct measure of corrosion, but short-lived excursions in operation of the plant are not identified. This includes sudden oxygen ingress, variations in corrosion inhibitor dosage or effects from changing service conditions (flow, temperature, pressure). Consequently, it is always advised to install one of the real-time monitoring techniques mentioned below together with corrosion coupons.

### **Galvanic probe**

The galvanic probe consists of two dissimilar metals that are electrically isolated from each other to facilitate measurement of the electrical current using a high-resolution amperemeter. Usually the metal pair include the pipework metal (steel) and a noble metal (brass), Figure 5.

In case of oxygen ingress, galvanic current will instantly run between the noble metal (cathode) and the steel (anode). If the brine on the other hand is completely deaerated, no current is measured. It is not possible to translate the measurement to the exact concentration of dissolved oxygen (DO), but since the system ideally should be deaerated, this semi-quantitative measure still provides valuable information.

While the galvanic probe is very sensitive to oxygen ingress (or oxidizing agents), it has limitations on other types of corrosion, such as CO<sub>2</sub>-corrosion, metal deposition or inhibitor dosage.

The galvanic probe should be inspected at half year intervals, when the geothermal plant is shut down for the summer period. If scaling is observed on the brass coupon (such as iron sulphide) it should be considered replacing it with another noble metal.

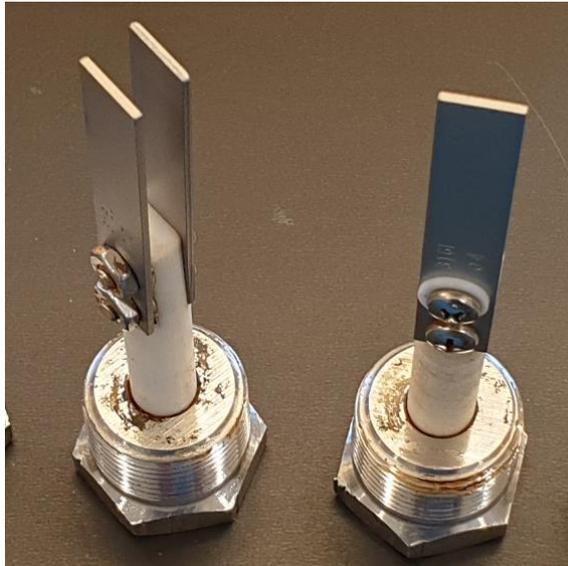


Figure 4. Corrosion coupons, strip type often installed in pairs.



Figure 5. Galvanic probe with brass and carbon steel coupons.

### ER probe

The ER probe (electrical resistance) measures the corrosion rate by detecting the gradual increase in electrical resistance of a metal element having a well-defined cross-sectional area. Any loss of metal due to corrosion will lead to an increased electrical resistance. The metal probe may be configured in several ways, as thin metal foil or a wire loop as shown in Figure 6.

Since the change in electrical resistance is extremely small and at the same time temperature dependent, the measurement is always accompanied by measurement on a fully enclosed and unexposed element in the probe. Today, high-resolution instruments are available so changes in corrosion rate over a day can be detected, provided the metal element has a sufficiently low cross-sectional area.

Corrosion rate can be calculated as mm/yr assuming uniform corrosion. If pitting occurs, this value may be slightly misleading but to the conservative side, still providing essential information. Readings from ER probes may also be interfered by formation of a conductive layer on the metal (e.g. iron sulphide), giving too optimistic values. Consequently, it is advised to inspect the probe at half year intervals, when the geothermal plant is shut down for the summer period. The examination should assess type of corrosion (uniform or pitting) and whether conductive scales are present on the probe.

### **Electrochemical probe**

Electrochemical probes are available in different configurations, including either two or three identical metal probes. However, the principle for measurement is basically the same. By applying a small electrical current amplitude on one probe using another passive probe, a rough measure for the electrode resistance is obtained. In this case, high resistance means a poor ability of the corrosion reaction to occur, previously introduced as eq. (1).

Using electrochemical principles such as LPR (linear polarisation resistance), the measured resistance can be transformed to an instantaneous corrosion rate (e.g. mm/yr). The obtained precision is usually within a factor 2-3 provided the measurement is not disturbed by e.g. deposition of conductive scales. The design of the probe is comparable with the galvanic probe in Figure 5.

### **Dissolved oxygen (DO) probe**

The DO probe provides a precise and instantaneous measure of the dissolved oxygen content in the brine. Since the expected levels in brine are in the range of 0 to 200 ppb (part per billion), high-sensitive sensors must be used. Such sensors are either based on galvanic measurement in a glass probe or optical measurement.

Due to the delicate sensing electronics, DO probes have limitations to temperature and pressure, and require frequent recalibration as opposed to the robust corrosion probes, mentioned above. For the same reason the DO probe is installed in special rig, providing depressurizing and cooling of the brine before measurement, Figure 7. The advantage of this rig is the possibility of connecting it to outlets of hot brine from the product well as well as the high-pressure lines downstream the injector pump.

As discussed above, ingress of oxygen has a tremendous impact on corrosion and possible particle release. This applies not only to unalloyed steel but also low-alloy stainless steel types such as 17Cr and 1.4401. Consequently, the installation of a DO probe is strongly recommended.

### **pH probe**

The pH probe should be installed in the same rig as the DO probe, because it has the same limitations to temperature and pressure as the DO probe.

Acidification of the brine may occur due to dissolved gasses (e.g. CO<sub>2</sub>) thereby presenting a risk of corrosion of especially unalloyed steel. Thus, pH should ideally be measured in the pressurized brine to include the effect of all dissolved gasses. However, such measurements require probes that are too complicated for continuous on-line monitoring. Therefore, the readings obtained from the rig in Figure 7 should be interpreted with care, because it can only show undesirable effects from e.g. chemical dosage or acid producing bacteria.

### ORP probe

The oxidation reduction potential (ORP) probe monitors the redox potential of the brine. It may be installed in the same rig as the DO probe and pH probe. Assuming fully deaerated conditions the reading from the ORP probe will show a constant low potential. On the other hand, unintended presence of oxygen or oxidizing agent will show an increase in potential that should be attended immediately because of the risk of corrosion.

Thus, the ORP probe provides largely the same information as the DO probe and galvanic probe. But the quantitative reading (mV) obtained with the ORP probe provides advantages in evaluating the risk of corrosion of passive metals, such as stainless steel. Since the stability of the protective oxide layer on stainless steel is very sensitive to the potential in the brine, it is possible to define critical threshold levels that require immediate attention in the operation of the geothermal plant.



Figure 6. Wire-loop for corrosion rate measurement by ER technique.



Figure 7. Automated water sampler for measuring DO, pH and ORP in cooled and depressurized brine.

### Other options for corrosion monitoring

Apart from the above techniques, other options for monitoring may be considered in the geothermal plant.

Iron count is frequently used in oil and gas installations to quantify corrosion. It involves regular sampling of the brine at one specific sampling-point, followed by measurement of the iron content in the water sample using chemical analysis. Ideally, the measured iron content should be correlated with a base-line sample

taken downhole at the production well to account for any iron in the reservoir. By this, any increase in iron content in the surface plant indicates corrosion of steel tubing.

The installed iron anodes in stainless steel canisters for filtering may also be useful to monitor corrosion. Logging the consumption rate is here recommended as indicative measure for corrosion. Additionally, installing a zero-resistance ampere meter between the anode and stainless steel can provide even more detailed information, similar to that obtained with the galvanic probe.

Non-destructive testing (NDT) may also be applied directly on the pipework to detect changes in the wall thickness. The applicable techniques include manual ultrasonic testing (UT), automated UT (T-scan) and radiography (RT). NDT performed at 1-2 year intervals in the exact same location provides an accurate measure for wall thickness and thereby corrosion rate of the pipework. Pipe bends and areas having turbulent flow conditions should be included in such inspection campaigns. These NDT techniques can be performed from the outside of the pipes while the plant is in operation, without any lost production.

Analysis of the particles collected in the filters may be considered too. An increasing amount of rust is here a direct measure for corrosion, but the analysis may also reveal other effects related to scaling (e.g. Ba, Ca), sand production, oily matter, bacteria or stability issues of the brine.

### **Layout and configuration**

The layout and configuration of the corrosion monitoring strategy should be based on a detailed review of the potential threats for each specific geothermal plant. A corrosion specialist should be consulted to undertake this task.

If steel is used as the main tubing material the need for corrosion monitoring is greater than that in plants having composite tubing installed. Likewise, the brine chemistry is decisive for corrosion, depending on presence of dissolved gases (e.g. CO<sub>2</sub>), metallic ions (e.g. Pb) and whether corrosion inhibitor is injected.

As a basis, we recommend one of the following configurations for different scenarios.

#### *Steel tubing for injection well*

Oxygen ingress in the surface plant is considered as the main risk.

- Install a side-stream loop downstream the injection pump
- Include corrosion coupons of steel
- Include at least one real-time corrosion monitoring technique connected with the SRO/Scada system, e.g. galvanic probe, ER probe, DO sensor or ORP sensor
- Define alert levels and follow-up procedures

### *Dissolved metal ions or CO<sub>2</sub>-gas in brine requiring corrosion inhibitor dosage*

Corrosion inhibitor is injected in the production well to deal with corrosion of steel caused by metal ions or CO<sub>2</sub>-gas in brine. In this case it is important to monitor corrosion to ensure correct inhibitor dosage at all times.

- Install a side-stream loop close to the production well manifold
- Include corrosion coupons of steel
- Include at least one real-time corrosion monitoring technique connected with the SRO/Scada system, e.g. ER probe or electrochemical probe
- Define alert levels and follow-up procedures

## **Interpretation**

Interpretation of corrosion monitoring data requires insight in plant design and operation as well as metals corrosion. During the first years of operation, it is advised to include a corrosion specialist for data analysis and interpretation due to the complexity of corrosion and geochemistry. At a later stage when baseline levels are defined and possible improvements have been implemented, interpretation and follow-up may be handed over to the staff, operating the geothermal plant. At this stage, detailed documentation should cover probe maintenance, alert levels and follow-up procedures on how to minimize corrosion in the geothermal plant.

## **9 References**

1. Holmslykke, H. et al. The risk of scaling and corrosion predicted from formation water composition for Danish geothermal plants. GEOTHERM final report in WP3. 2019.
2. Mathiesen, T. et al. Results of on-site monitoring campaign and parametric laboratory testing. GEOTHERM Milestone Report M5.4. 2019
3. Guide de bonne pratique d'un forage géothermique en aquifère profond en Ile-de-France/French guidelines. Geothermie perspectives website. 2018.
4. NACE Standard, SP0499-2012-SG. Corrosion Control and Monitoring in Seawater Injection Systems. 2012.
5. Salvage of U864 - Supplementary Studies - Study No. 1: Corrosion, Technical Report, Det Norske Veritas, Report No. 23916-1, 2008.