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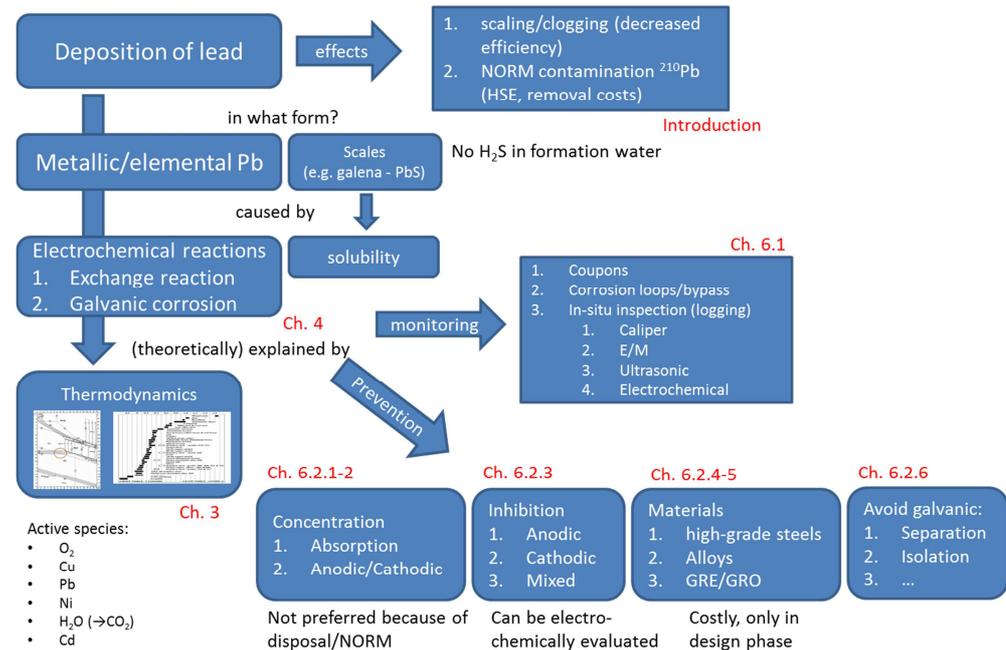
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Summary



Motivated by operational problems in one of the Dutch geothermal doublets, a technology cluster was started to investigate the electrochemical reactions between the metal parts of a geothermal installation and the formation water, which can lead to the deposition of lead.

The focus in this study was on the doublets in the Slochteren formation. In this formation, significant lead concentrations are found (among other causes due to the exchange of elements with the overlying Kupferschiefer formation).

Theory and own analysis by the geothermal operators suggest that the deposition of lead in their systems concerns metallic lead, indeed caused by electrochemical reactions in the system:

- (Electron) exchange reactions between the lead in the formation water and the iron in the casings
- Galvanic corrosion, in which lead deposits on the least noble of two metal in a conductive connection

Several monitoring techniques are described, including coupons, corrosion loop and in-situ inspection tools.

Recommended measures to prevent corrosion and/or lead deposition can be divided into three categories:

- Material selection (often not practical because of high costs; often only applicable in the design phase of a project)
- Corrosion inhibitors (used and effective; in this reports, recommendations are made for evaluation of different inhibitors)

Concentration of the deposits by absorption of anodic/cathodic protection (not preferred, because of problems with the disposal of the radioactive deposits

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1 Introduction and scope

1.1 Technology cluster lead deposition

Motivated by operational problems caused by the deposition of lead in one of the Dutch geothermal doublets, a so called technology cluster (TC) was started on this topic early 2014. Lead deposition forms a risk to the operation of geothermal doublets because it can lead to scaling (and clogging) and thereby to decreased efficiency. Furthermore, the disposal of lead scales comes with HSE (health, safety and environment) concerns and costs due to the radio activity of the natural occurring Pb-210 isotope.

In a TC, TNO aims to provide the sponsoring participants with the knowledge to answer a number of research questions, upon which the participants can improve their operations or business. Also, general and specific recommendations are made. In this TC, the following questions have been investigated:

- Which (electrochemical) interactions between the (salt) formation water and the different components of a geothermal installation can cause deposition of metals, lead in particular, in the installation?
- What can be monitored in a geothermal installation to determine whether the identified reactions are relevant for the specific installation, or to determine the effect of these interactions?
- What can be done to avoid undesired reactions and what is the practical feasibility of these solutions?

1.2 Focus on Slochteren formation

The participants of this technology cluster are all in some way involved in (possible future) geothermal energy production from doublets in the Slochteren formation, which is present in the Northern part of the Netherlands in the (Upper) Rotliegend lithostratigraphic unit. In this formation, lead concentrations in the formation water are significant. The overlying Kupferschiefer formation, which can easily exchange elements with Slochteren due to several juxtapositions, but also the Carboniferous coals can be the source of the lead in the Slochteren formation water.

For the processes and reactions described in this study, formation water characteristics such as composition, pH and temperature, are important parameters. In the investigations, values and value ranges for these parameters have been chosen that are relevant for the Slochteren formation (see Chapter 2).

1.3 Setup of this report

In Chapter 3, the theoretical background behind electrochemical reactions that may occur in geothermal system is explained. Chapter 4 focuses on the redox potentials of ions that are found in the Slochteren formation water. These potential are the driving force behind the actual electrochemical reactions described in Chapter 5. Finally, Chapter 6 focuses on monitoring tools and possible measures to prevent or mitigate the risks involved with lead deposition. This report contains three restricted

appendices, that are made available to the participants of this technology cluster only.

2 Formation water composition for the Slochteren reservoir

Table 1 presents an overview of the spread in the formation water composition for the Slochteren reservoir. The minimums and maximums in g/l are based on two or eleven measurements for geothermal wells and maximum eight measurements from gas fields. All analyses showed the presence of sodium, potassium, calcium, magnesium, and chloride. For all other elements there is less data available. Remarkable, but fortunate, is the absence of H₂S in this formation water. The absence of H₂S is confirmed by the formation water composition data that were provided by a number of participants in this technology cluster. The measured pH ranged from 4.8 to 6.5 with a temperature of minimum 70°C up to 94°C. It has been agreed with the operators involved in this technology cluster to assume the values below to be representative for their own situations.

Table 1: Formation water composition for selected samples in the Slochteren reservoir

element	min (g/l)	max (g/l)
Na	40	110
Mg	0.5	5
Al	0.005	0.01
K	0.4	110
Ca	0.5	35
Mn	0.005	0.01
Fe	0.05	0.2
Ni	0.00005	0.0001
Cu	0.00005	0.0002
Zn	0.02	0.03
Sr	0.2	0.7
Cd	0.001	0.002
Ba	0.003	0.006
Pb	0.002	0.003
HCO ₃ ⁻	0.01	0.07
Cl	80	190
SO ₄	0.2	0.6

3 Theoretical background

In this chapter we focus on theoretical background of electrochemical reactions. To do this we first have a look on what we can learn from so called Pourbaix diagrams in paragraph 3.1. These diagrams can tell us which electrochemical reactions are possible based on thermodynamic calculations. Then, using the relevant data from the Pourbaix diagrams, it is shown in paragraph 3.2 how using the Nernst equation we are able to calculate the actual redox potentials at the given temperature and concentration. The theory is explained using iron as an example. In Chapter 4, the outcome of these calculations will be shown for the composition of the Slochteren formation water.

3.1 How to read Pourbaix diagrams

Pourbaix diagrams [1], also known as a potential/pH diagrams, show the possible stable equilibrium phases of a specific aqueous electrochemical system at a set temperature (mostly at 298K). Predominant ion boundaries are represented by lines. As such, a Pourbaix diagram can be read much like a standard phase diagram with a different set of axes. Similarly to phase diagrams, they are completely based on thermodynamics and therefore do not give information about reaction rates or kinetic effects.

All Pourbaix diagrams used in this report are drawn up for aqueous solutions at 298K showing the potentials with respect to the standard hydrogen electrode (NHE). In all diagrams two diagonal (dashed) lines marked (a) and (b) indicate the area in which water is thermodynamically stable. The area below the line marked (a) is where water will be reduced and hydrogen gas will be formed. Depending on the pH of the electrolyte the corresponding reaction can be written as:



or



The corresponding equilibrium potential for these reactions can be written as:

$$E_0 = 0.000 - 0.591\text{pH} - 0.0295 \log(p_{\text{H}_2}) \quad (\text{V}) \quad (3)$$

The area above the line marked (b) in the Pourbaix diagram is where water will be oxidized and oxygen gas will be formed:



Since this is an equilibrium it also indicates the strength of oxygen as an oxidizing agent. The corresponding potential for this equilibrium is:

$$E_0 = 1.228 - 0.0591\text{pH} + 0.0147 \log(p_{\text{O}_2}) \quad (\text{V}) \quad (5)$$

As an example, Figure 1 shows the Pourbaix diagram of iron in water at 298K. Besides the already mentioned (a) and (b) lines indicating the water stability there are several other equilibrium lines visible. The diagram shows that metal iron (Fe) is not a stable phase over the complete pH region from pH -2 to +16. In an acidic environment iron will oxidize to form Fe^{2+} (lines 23) while at more alkaline conditions the hydroxide $Fe(OH)_2$ is formed (line 12). Above pH 14 $HFeO_3^-$ can be found. The diagram also indicates which phases are solid and which are dissolved in the aqueous solution. At low pH the stable phase Fe^{2+} will be dissolved in the solution, while at higher pH the iron hydroxide phase will form a (passive) film on the iron substrate.

The diagram also shows that when a potential is applied to the system, either by an external power supply or through the presence of other electrochemical active species, other iron phases can be in equilibrium. At low pH and at higher potentials the Fe^{2+} will oxidize further to Fe^{3+} and at higher pH $Fe(OH)_2$ can be oxidized to $Fe(OH)_3$.

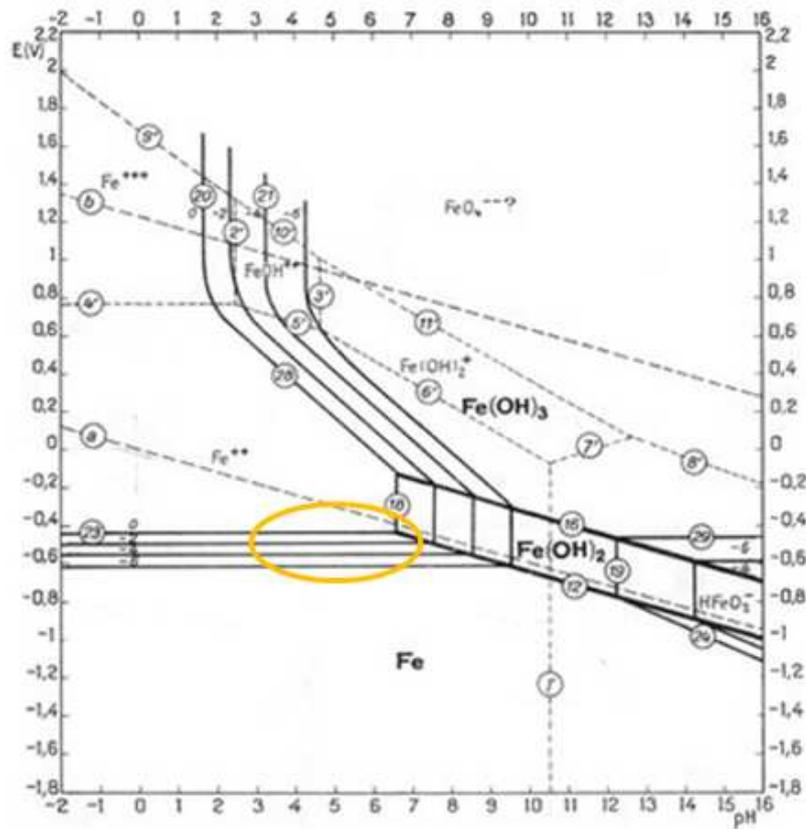


Figure 1: Pourbaix diagram for the system iron-water, at 25°C; source: <http://www.wetenschapsforum.nl/index.php/topic/181404-redox-reacties-en-pourbaix-diagram/>

The orange circle in the iron Pourbaix diagram indicates the situation for iron in contact with the Slochteren reservoir formation water (at 298K) with a pH between 4.8 and 6.5 (paragraph 2.1). In this case we assume no presence of an external power supply. The diagram shows that in this pH region the iron metal phase is

instable as it is below the reduction potential water. In other words, due to the reduction of water (equation 1) the iron can be oxidized (lines 23):



In the diagram this equilibrium potential is indicated by reaction 23 and by 4 parallel lines marked with a value of 0, -2, -4 and -6. This number indicated refers to the logarithmic concentration of Fe^{2+} in the solution. The parallel lines show the change in equilibrium potential upon the concentration of Fe^{2+} in the electrolyte. The potential corresponding to the line for a concentration of 1M of Fe^{2+} (marked with the value 0) is referred to as the standard equilibrium potential which is -0.44V versus NHE.

3.2 The Nernst equation: determine the influence of temperature and concentration

The equilibrium potential or half-cell potential at a given concentration and temperature can be calculated using the Nernst equation [2] and the relevant standard equilibrium potential determined from the Pourbaix diagram:

$$E = E^{\circ} - \frac{RT}{nF} \ln \left(\frac{a_{red}}{a_{ox}} \right) \quad (7)$$

In which:

- E half-cell or equilibrium potential at the temperature of interest
- E° standard equilibrium potential
- R universal gas constant: $R = 8.314\text{J}/(\text{K}\cdot\text{mol})$
- T absolute temperature (K)
- a chemical activity/concentration for the relevant species (mol/l)
- F Faraday constant: $F = 96485\text{C}/\text{mol}$
- n number of electrons transferred in the half-reaction

As an example we look again at the iron case described above and calculate the half-cell potential at a temperature of 80°C (353K) and an Fe^{2+} concentration of 0.2g/l which is the maximum concentration as observed for the Slochteren formation water (Table 1). As shown in the previous paragraph the standard equilibrium potential determined from the Pourbaix diagram of iron in the relevant pH range is -0.44V vs NHE for the reaction shown in Equation 6. Since two electrons are involved in this reaction n equals 2. The concentration of the oxidized species (Fe^{2+}) can be calculated using the molecular weight of iron (55.8g/mol). The 0.2g/l corresponds to 3.6e-3mol/l. Since in this case the reduced species is the solid state iron we can neglect its concentration and re-write the Nernst equation to:

$$E = E^{\circ} + \frac{RT}{nF} \ln(a_{ox}) \quad (8)$$

Using the above values the equilibrium potential at 80°C and 0.2g/l Fe^{2+} is calculated to be -0.526V vs NHE.

4 Redox potentials of the ions in the Slochteren formation water

4.1 Sequence of oxidizing strength

Similar to the example given for iron in the previous chapter, the Pourbaix diagrams [1] were investigated for all other ions present in the Slochteren formation (see Table 1 in Chapter 2). Figure 2 shows the standard equilibrium potentials for the various ions, which corresponds to the equilibrium potential at an ion concentration of 1M at 25°C, determined directly from the Pourbaix diagrams between the for the Slochteren formation water relevant pH range of 4.8 to 6.5.

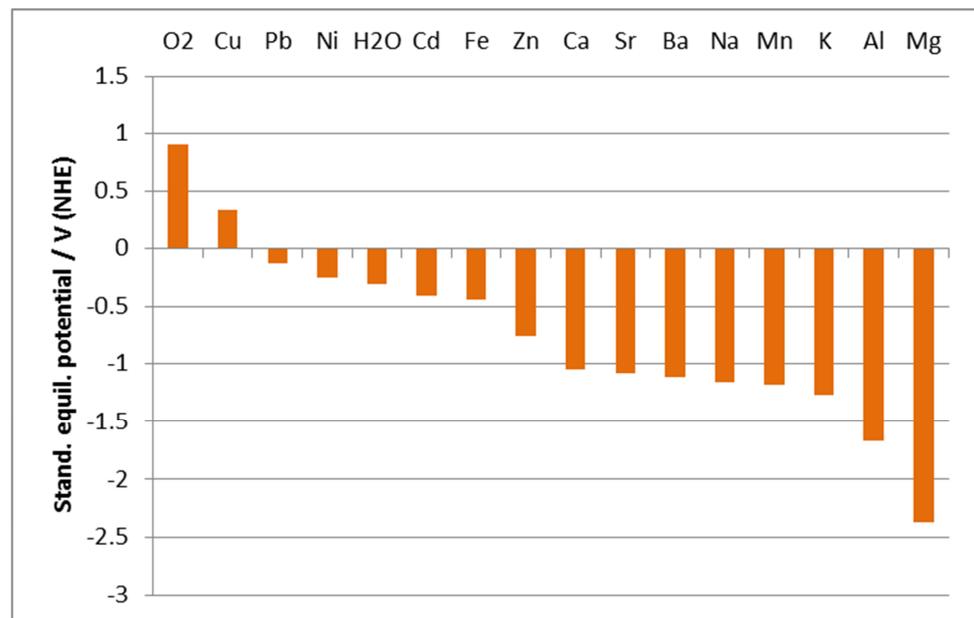


Figure 2: Plot showing the standard equilibrium potentials for the ions observed in the Slochteren formation. Oxygen is added to show the strength of this oxidizing agent.

The sequence shown in Figure 2 indicates the oxidizing strength of the ions. The species on the left hand side of the plot have a strong oxidizing strength which means that they are thermodynamically able to oxidize the species which are depicted on the right of them. It is clearly shown that oxygen is by far the strongest oxidizing agent. If oxygen would be present in the formation water it would thermodynamically easily be able to oxidize iron based installation materials. Similar copper, lead, nickel, water (protons) and even cadmium could in principle oxidize iron. One should however realize that, as is emphasized in the previous chapter, the standard equilibrium potentials are completely based on thermodynamics and therefore do not allow for reaction rate or kinetic effects.

The species on the right hand side of the graph are the reducing agents (Zn, Ca, Sr, Ba, Na, Mn, K, Al, Mg). Since these species have a redox potentials more positive than the reduction potential of water, they are only stable in their oxidized form and can therefore be neglected as being electrochemically active.

Using the relevant standard equilibrium potentials, the corresponding redox potentials were calculated using the Nernst equation at the relevant temperature of 94°C and the maximum ion-concentration (see Table 1). Since oxygen is not present in the formation water it is also not further investigated. Figure 3 shows the temperature dependence of the redox potentials for the (most) electrochemically active species in the formation water.

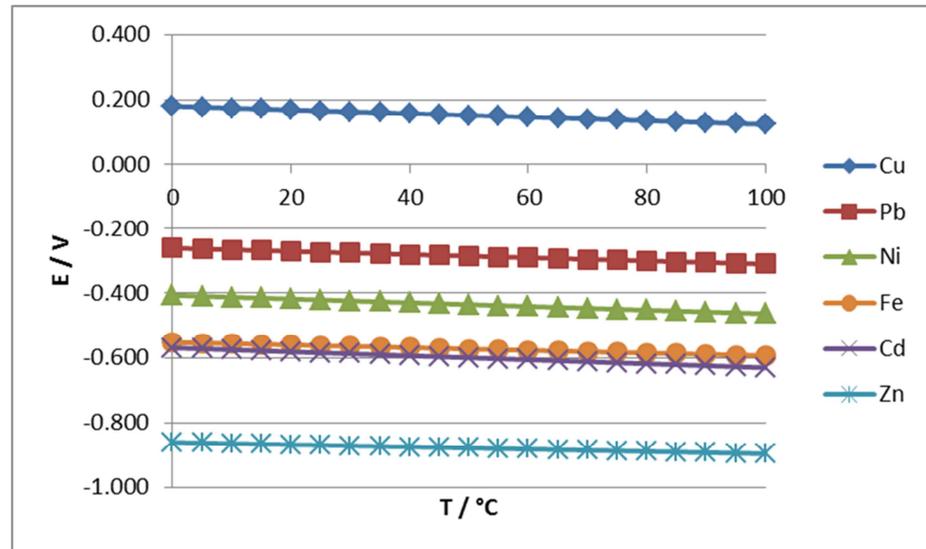


Figure 3: Temperature dependence of the redox potentials as calculated with the Nernst equation using the maximum concentration observed in the Slochteren formation water

From this plot we can conclude that Cu, Pb and Ni have the electrochemical power to oxidize iron. As mentioned above this observation is only based on thermodynamic calculations. The reaction rate depends on kinetics. Since the concentration of Cu and Ni in the formation water is in the order of at least 100 times less than that of Pb, we can assume that Cu and Ni will have a much lower impact.

4.2 (Electro)chemical reactions of Naturally Occurring Radioactive Material (NORM)

This study focusses on the electrochemical deposition of stable lead and the radioactive element of the uranium series, lead Pb210. Other natural occurring radioactive material (NORM) in the brine of the Slochteren formation can be radium (Ra), radon (Rd) and kalium (K) which are products of the uranium series. To a much lesser extent decay products of the thorium series are detected. Both uranium and thorium are not mobile and do not contribute to the NORM found in these geothermal brines. The electrochemical activity of lead will be further discussed upon in the next chapter. The Pourbaix diagram of radium [1] shows that the electrochemistry of this element can be neglected as the standard equilibrium potential is very negative (-2.9V). Radium could however chemically be substituted for barium, strontium and calcium in deposits in BaSO₄ (barite), SrCO₃ (strontianite), SrSO₄ (celestite/celestine), CaSO₄ (anhydrite). Similar can be stated for kalium. For the evaluation of chemical precipitation (scaling) of these products we refer to [10].

This report focusses on the electrochemical precipitation of stabile and radioactive lead (and copper).

5 Electrochemical reactions in the geothermal installation

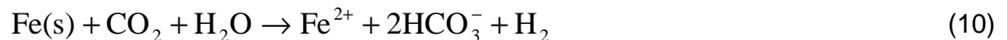
In this chapter, we focus on electrochemical reactions that might occur in the geothermal installations using the formation water of the Slochteren reservoir. In the first two paragraphs the situation is discussed for low grade steels. Section 5.1 discusses the corrosion due to dissolved carbon dioxide in the formation water. In the second paragraph, lead deposition due to an electrochemical exchange reaction is discussed. Electrochemical reactions as a consequence of galvanic element formation due to the electrical contact of two different steel types in contact with the formation water is discussed in section 5.3.

5.1 Carbon dioxide corrosion of the steel casing

While dry CO₂ is not corrosive, CO₂ in combination with water creates an acidic environment that causes corrosion of steels [4]. Equation 9 shows the proton formation due to the dissolution of carbon dioxide in the formation water:



As a consequence of this reaction, the pH of the formation water decreases (pH observed between 4.8 and 6.5). In the previous chapter we already showed that at these potentials protons (eq. 1) can be reduced to form hydrogen at the expense of iron to be oxidized (eq. 6). Thus, at the steel/liquid interface, an anodic reaction takes place and iron atoms are oxidized as cations. At the meantime, a cathodic reaction takes place and protons are reduced. The overall electrochemical reaction is:



The present bicarbonate and carbonate anions can react with ferrous ions to form an iron carbonate film. This carbonate film can under ideal circumstance be able to prevent the iron below for further oxidation and thus stop the corrosion process. If the hydrogen gas evolved during this reaction is detected it can be used as an indicator for carbon dioxide corrosion of the steel.

The corrosion rate of (casing) steel is investigated especially for down hole CO₂ storage where the CO₂ concentration in the injection wells is much higher and the water content much lower than in the case of geothermal wells. It is shown that for down hole storage the corrosion rate depends on various variables: pressure, temperature, the presence and quality of well cement, salts and chemicals in the brine, pH etc. [4]. For these types of systems it is often observed that the initial high corrosion rate decreases in time due to the formation of the passivating iron carbonate layer.

It is however very unsure if a good quality corrosion inhibiting iron carbonate layer is also formed under the conditions used in geothermal installations. Figure 4 shows an chemical equilibrium calculation for the system water, iron and carbon dioxide in the pH region 4 to 7, relevant to the Slochteren formation. This plot which is based on thermodynamical data shows that in the pH region below 6 the dissolved carbon dioxide will be present in the form of H₂CO₃ and most of the dissolved iron will be in

the form of Fe^{2+} . Only at a pH close to 6 the concentration of the HCO_3^- species starts to rise causing the formation iron carbonate to be the predominant iron species at a pH larger than 6. From this one could conclude that an iron carbonate layer will be formed at a pH above 6. As mentioned already above these calculations are based only on thermodynamic values and will therefore not allow for reaction rate or kinetic effects. Even if a carbonate layer is formed it is uncertain if this layer has the quality and morphology to protect the underlying iron for further corrosion. It will therefore be very important to monitor the corrosion rate of the bare steel.

The above stated pH dependence of iron-carbonate scaling is also the outcome of tests reported in reference [8] and [9]. On the basis of this information the iron-carbonate scaling in the evaluated producer and injection wells is not likely to result in pseudo passivation of carbon steel.

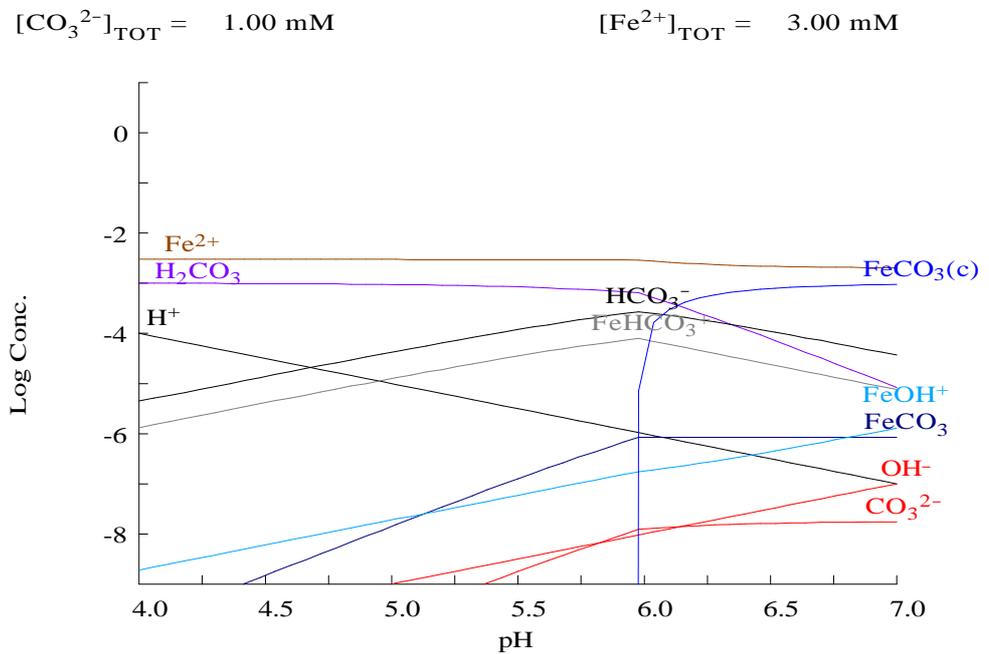


Figure 4: Chemical equilibrium calculation for the system water, iron and carbon dioxide.

Although the formation of a good passivating iron carbonate layer is unlikely based on the pH and concentrations of iron and carbonate in the bulk of the formation water there might be special conditions/occasions which could result in a good passivating layer. For instance during drilling the drilling fluid has a much higher pH and also contains inhibitor. This might after rinsing with formation water result in a thin passivating layer of iron carbonate, inhibitor or both. Due to corrosion of the tubing the concentration of iron and carbonate species could be different close to the tubing wall with respect to the bulk concentrations. These local conditions could be much more favourable for iron carbonate formation than those based on the bulk concentrations.

5.2 Lead deposition due to an exchange reaction

Figure 5 illustrates the Pourbaix diagram of lead in water at 25°C. The orange circle in this plot shows the relevant pH area. The equilibrium reaction in this area is the reduction of lead ions to metallic lead:



As shown in Figure 3 of Chapter 4, the Nernst redox potential for this equilibrium can be calculated for the specific lead concentration at the temperature of the formation water. It is shown that for the complete temperature range of 0 to 100°C the redox potential of the lead reduction is higher than that of iron. Therefore it can be concluded that thermodynamically lead ions are able to oxidize metallic iron. This type of reaction is often referred to as an exchange reaction. The more noble metal (lead) is deposited and the lesser noble metal (iron) is dissolved. The overall equation for this exchange is:



Figure 6 shows the very small, only a few mV, temperature dependence of the cell potential for the exchange reaction of lead with iron between 0 and 100°C.

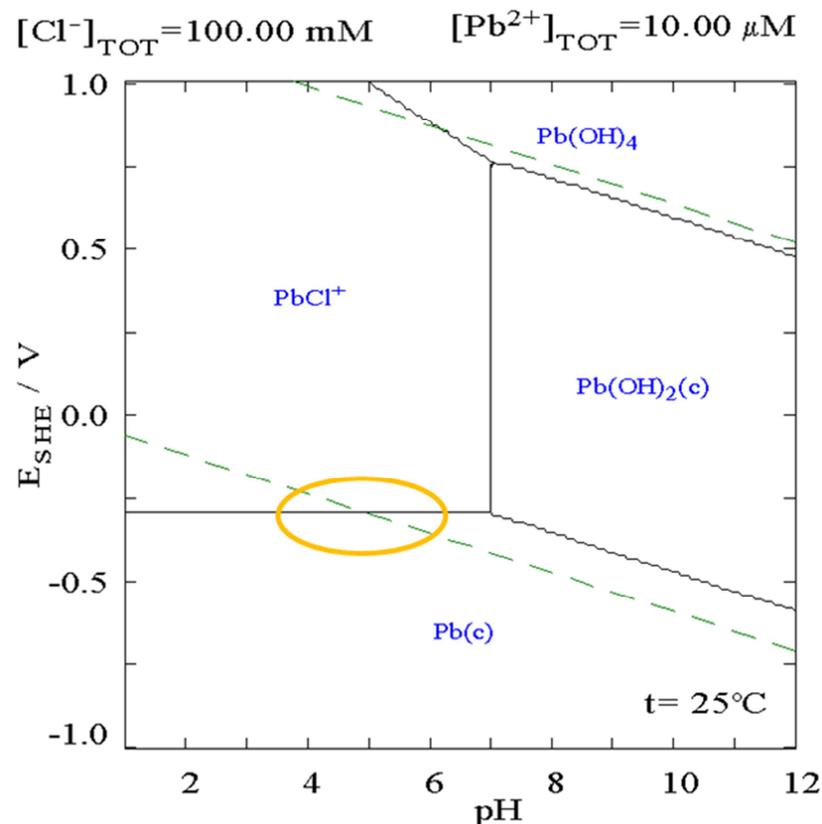


Figure 5: Pourbaix diagram for the system lead-water, at 25°C. The orange circle shows the relevant E/pH equilibrium reaction area. Source: http://en.wikipedia.org/wiki/Compounds_of_lead

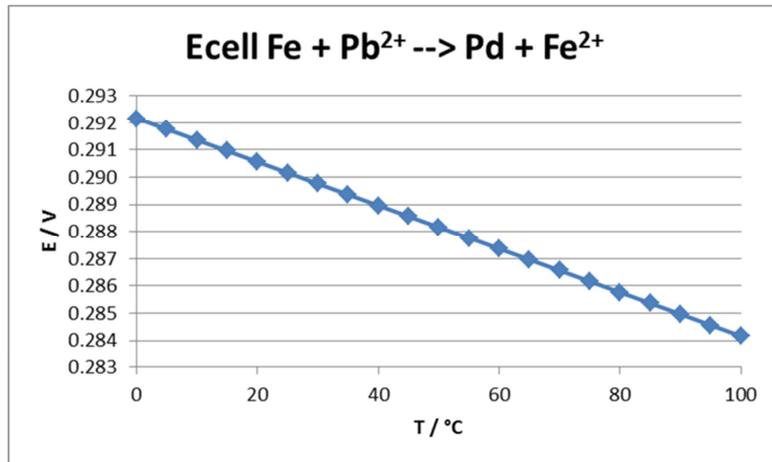


Figure 6: illustrates the very small temperature dependence of the cell potential for the exchange reaction of lead and iron.

An example of a lead deposit on low grade steel is given by Hartog et al. [3] who observed lead deposits, with thicknesses of 10mm or more, on steel casings in Dutch natural gas systems. Figure 7 shows a cross-section scanning electron microscope graph of such a deposit. A schematic drawing of the situation and their explanation is given in Figure 8.

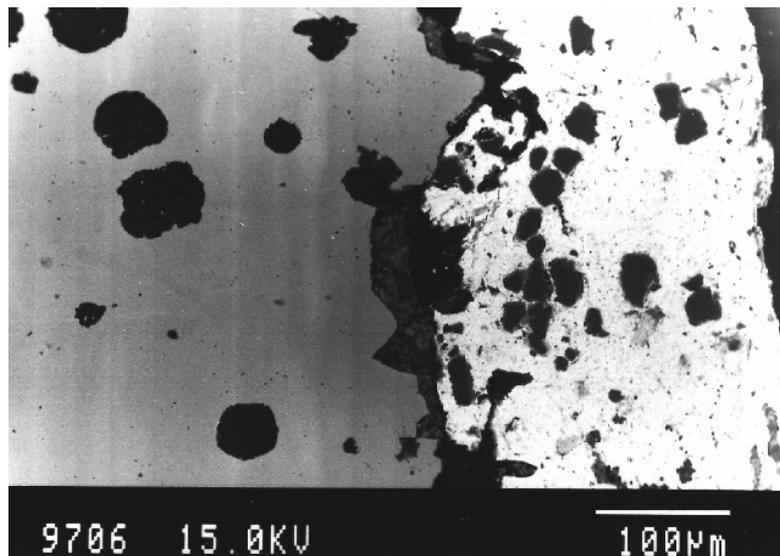


Figure 7: SEM cross-section photograph showing elemental lead on an iron surface (figure from Reference [3])

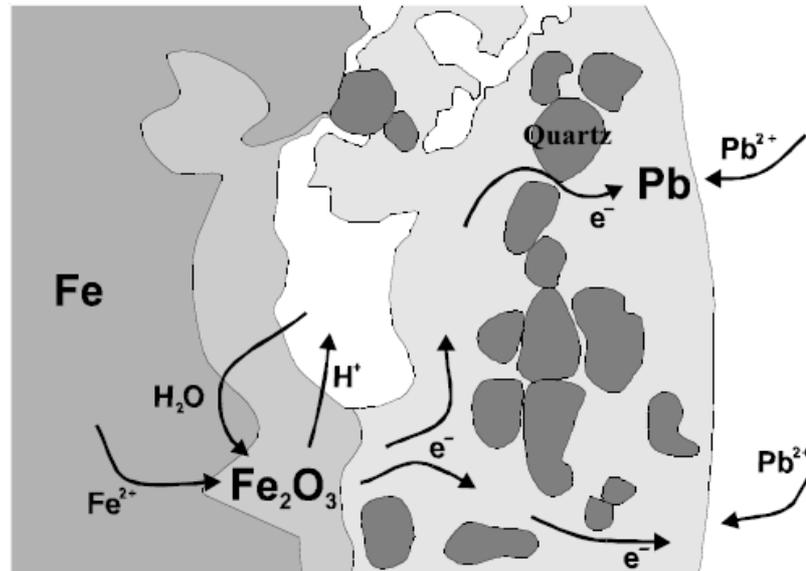


Figure 8: Schematic drawing of the situation and the electrochemical reaction observed in Figure 7 (figure from Reference [3]).

The metallic lead deposits can, when in contact with air, convert into secondary lead minerals.

As mentioned in paragraph 4.1, both Cu and Ni could deposit on the steel due to an exchange reaction, similar as lead. The much lower concentration of Cu and Ni could be the reason that this type of deposit is not (yet) observed in practice in the Netherlands (Cu deposits do show in German geothermal wells in the Slochteren formation and this is possibly linked to the Cu content of the Kupferschiefer).

5.3 Galvanic element formation

Up to this point electrochemical reactions are discussed between the low grade iron tubing of the installation and electrochemical active species in the formation water. In this paragraph we focus on the risk of using different types of steel in direct, electrical contact with each other. Figure 9 shows a schematic plot of the use of two different installation materials A and B in contact with the formation water (electrolyte) in the case where the two metals are electrically disconnected by the use of for instance a spacer.

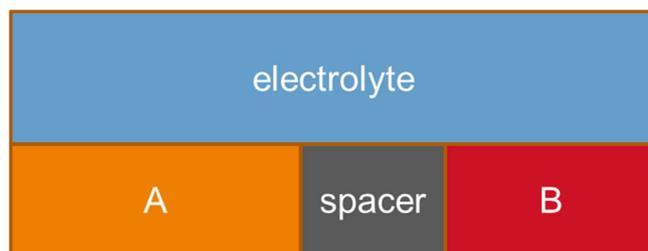


Figure 9: Situation where two different types of metal are used which electrically disconnected.

In this case both materials will be in an independent equilibrium with the electrolyte. The equilibrium potential will depend on the material itself (composition and morphology) and the interaction with the electrochemical active species in the electrolyte. Thus the equilibrium potential, also called the open-circuit potential, of interfaces A/electrolyte and B/electrolyte can be at different value.

Figure 10 shows the so-called galvanic series for the situation in sea water at 25°C. The values at the x-axis are the open-circuit potentials of the metals with respect to a saturated calomel reference electrode (SCE). On the bottom left are the very noble metals as gold and platinum while at the top on the left the very reactive metals like zinc and magnesium can be found. The graph shows that for these conditions there is a large difference of ~0.5V between for instance the often used stainless steel 316 (~ -0.1V) and low alloy steel (-0.6V).

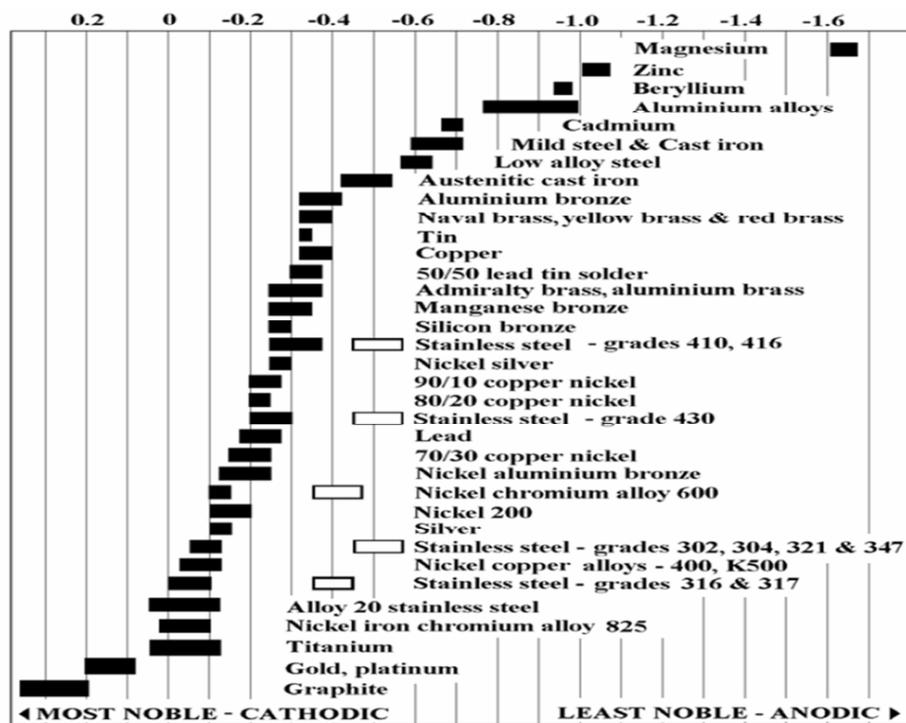


Figure 10: Galvanic series for sea water at 25°C.

Figure 11 shows the situation in which two materials A and B are not separated, but in a direct electrical contact with each other.

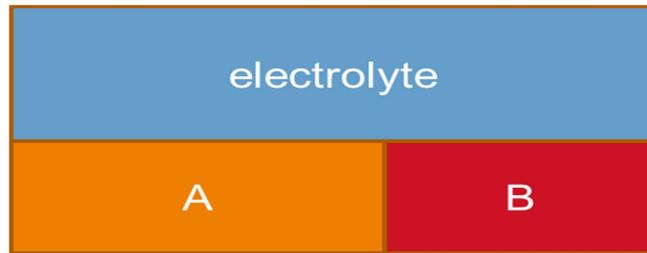


Figure 11: Situation in which two different types of metal are used in direct electrical contact.

In this case presented in Figure 11, both materials will be forced to be at the same equilibrium potential. The value of this mixed potential will be somewhere between the two individual equilibrium potentials and it will depend on the ratio between the surface areas of the two metals in contact in what extent it will move to one or the other direction. This mixed open-circuit potential however will polarize both metals away from their individual equilibrium potentials. This effect is called galvanic element formation and will make one of the metals more anodic and the other more cathodic than their individual equilibrium potentials.

Due to this polarization electrochemical reactions can occur in which both metal/electrolyte interfaces are involved while the necessary electrons are transported over the metal/metal interface. It should also be pointed out that galvanic corrosion does not only occur in water. Galvanic cells can form in any electrolyte, including moist air or soil, and chemical environments.

A well-known example of this effect is the so-called galvanic corrosion in which on the most noble metal a reactive species is reduced (oxygen, or protons) while the less noble metal is oxidized (corroded). The involved electrons are transported over the interface between the two metals.

When using the galvanic series, as shown in Figure 10, to explain observations made in geothermal installations we should be aware that most of the galvanic series are made after measurements of the open-circuit potential of the materials in seawater at 25°C. This is a completely different condition as will be the case in a geothermal installation. In the latter the temperature is much higher, even after the heat exchanger. But most of all, the composition of the electrolyte is completely different, most important the absence of dissolved oxygen. Furthermore one should not forget that often inhibitors are used in geothermal installations that can have a great impact on the equilibrium potentials and might react differently for different materials.

It is unlikely that the situation in a geothermal installation would change the order observed in the galvanic series, but it could well be that the potential differences are significantly different, mainly due to the absence of oxygen in the formation water. It would therefore be interesting to construct a galvanic series plot for geothermal installations using the Slochteren formation water. To do so the open-circuit potential should be measured (w.r.t. a reference electrode) on electrically insulated work pieces in contact with the formation water (preferably in-situ) for each of the materials applied in geothermal installations. For this one should use a potentiostat or a high-ohmic volt-meter and measure the potential with respect to a reference electrode which is placed in the water in close vicinity of the material of interest.

5.4 Lead deposition due to galvanic element formation

In the case of a geothermal installation, in the absence of oxygen, using two different metals in electrical connection (for instance SS316 and low grade steel) another reduction reaction should take place on the more noble metal. For this reaction the stronger oxidizing agents, Cu, Pb, Ni and protons (see paragraph 3.2) are available. The high concentration of lead ions in the Slochteren formation water makes it likely that the Pb^{2+} can be reduced on the negatively polarized metal (in this case the SS316). As a consequence metallic lead can be deposited on the noble metal while the least noble metal, in this case the low grade steel, will be positively polarized and therefore corrode.

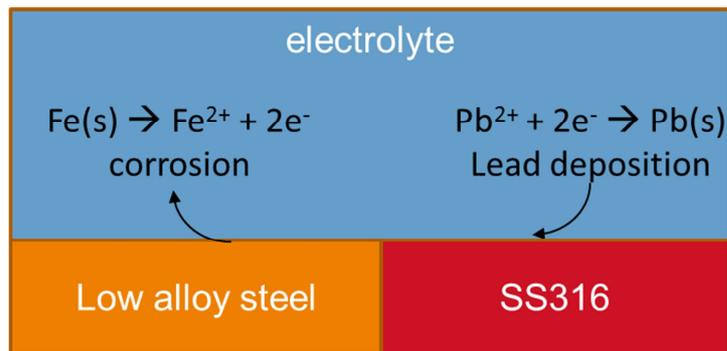


Figure 12: Schematic presentation of lead deposition due to the galvanic element formation for stainless steel in contact with a low grade steel. While the low alloy steel corrodes, lead is deposited on the SS316. The necessary electrons are transported over the metal/metal interface.

One could also argue that lead deposited initially through the exchange reaction discussed in paragraph 5.2 automatically leads to the formation of two metals, steel and lead, in electrical contact. So after an initial deposition of lead through the exchange reaction the further deposition could be taken over by the galvanic element formation. In this case the lead will be deposited on the more noble metal being lead while the steel will corrode.

As mentioned already for the exchange reaction both Cu and Ni could deposit on the steel, similar like lead. The same could be foreseen for the deposition due to galvanic element formation. The much lower concentration of Cu and Ni could be the reason that this type of deposit is not (yet) observed in practice in the Netherlands (Cu deposits do show in German geothermal wells in the Slochteren formation and this is possibly linked to the Cu content of the Kupferschiefer).

6 Measures against lead deposition / corrosion

In this chapter we look at what can be done to avoid corrosion of the geothermal installations and the deposition of lead. Besides technical measures to avoid corrosion and lead deposition also some monitoring tools will be discussed upon briefly.

6.1 Monitoring tools

A good overview of monitoring tools for corrosion problems is given by Zhang et al. [4], as well as by NACE [12]. Since corrosion of steel and lead deposition are coupled phenomena in geothermal installations using the Slochteren formation water we have selected some of the monitoring techniques and describe the use of these tools below for monitoring corrosion and lead deposition.

6.1.1 *Coupons*

Coupons can predict the following types of corrosion when correctly emplaced to ensure appropriate exposure: general corrosion, crevice corrosion, pitting, stress corrosion cracking, embrittlement, galvanic corrosion, and metallurgical structure-related corrosion. However, coupons have several limitations. An extended period of time is required to produce useful data, and coupons can only be used to determine average corrosion rates. Furthermore, corrosion coupons can only measure corrosion in the part of the well in which they are placed. Corrosion coupons can also be used to investigate the lead deposition rate and/or scaling. Coupons can also be used to study the rate of deposition of lead. After the exposure time the amount of deposited lead can be determined either measuring locally the amount of deposited lead by X-ray fluorescence or by dissolving the lead and measuring the concentration using an elemental analysis tool like ICP-AES (Inductively coupled plasma – atomic emission spectroscopy) or AAS (atomic absorption spectroscopy).

6.1.2 *Corrosion loops/bypass*

A corrosion loop is a section of tubing that is valved so that some of the stream is passed through a small pipe running parallel to the injection pipe at the surface of the well. Because the composition of this pipe is the same as the well tubing, it acts as a small-scale version of the well; which can more easily be monitored on corrosion and lead deposits.

6.1.3 *In-situ inspection tools*

There is an extensive list of in-situ inspection tools called logs. Caliper logs, also known as multifinger calipers, measure the internal radius of the casing in several directions by using multifinger feeler arms of the tool. Electromagnetic thickness logs are one of two available electromagnetic measuring methods for corrosion monitoring. These logs are carried out by electromagnetic induction tools. Magnetic flux logs make use of magnetic flux leakage (MFL) technology to determine the location, extent and severity of corrosion and other metal loss defects in tubulars. Near locations of defects such as corrosion or pitting, some of the flux leaks out of the pipe, and these leaks are detected by the tools sensor arrays. Ultrasonic

corrosion logs employ a very high transducer frequency to measure anomalies in the tubing or casing. The emitter sends out sound waves and the detector measures the reflected response. The survey can measure anomalies as small as 0.3 inches and measures anomalies both on the inner and outer surfaces of the tubing or casing. Logs or a combination of simultaneous performed logs, can also be used to detect scaling/precipitates on the inner tubing. Using a gamma-ray (GR) measurement log it is possible to detect scaling of radioactive material.

Table 2 gives an overview of the suitability of electrochemical sensors for corrosion detection. Electrochemical noise measurements (ENM), electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) have been used extensively in downhole wireline corrosion monitoring at oil wells. Figure 13 shows the schematic set-up for on the left EIS and LPR measurements and on the right for electrochemical noise measurements. These measurements could also be performed ex-situ. In that case one has to be sure that the electrolyte resembles as much as possible the formation water. The best way would be to use formation water from the a geothermal site. Oxygen should be expelled from this electrolyte by bubbling nitrogen through the water before the experiments and keeping it in nitrogen atmosphere during the experiments. The pH of the electrolyte should be set by bubbling carbon dioxide gas through the electrolyte while measuring the pH. The use of these methods for the in-situ detection of lead deposition is not straight forward and is to our knowledge not published.

The detection of galvanic element formation due to electrical contact of two different materials is not straight forward. Using in-situ open-circuit potential (OCP) measurements, which measures the potential difference of the material with respect to a reference electrode close to the metal/liquid interface, one could determine local potential differences in-situ. This however will not identify if the materials are connected or separated by for instance a spacer.

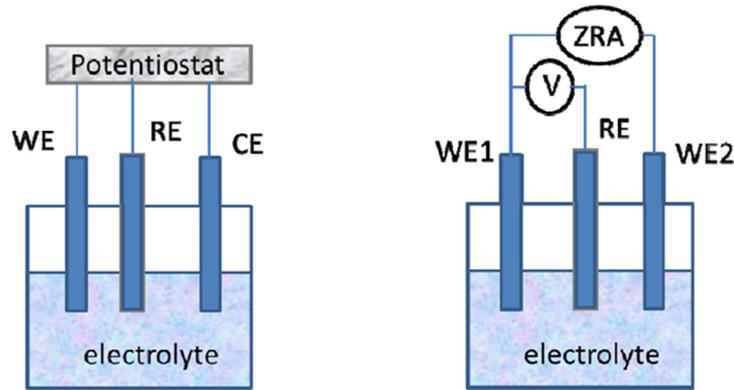


Figure 13: schematic presentation of the set-up for electrochemical measurements. On the left-hand side is the set-up depicted for impedance and the linear polarization resistance measurements. On the right-hand side is the set-up for electrochemical noise measurements. WE is working electrode (material you want to investigate); RE is reference electrode, for instance a Ag/AgCl or a saturated calomel electrode (SCE) and CE is the counter electrode, which normally is a large area electrode. In the case of noise measurements two working electrodes are used of the same material

Table 2: Characteristics of LPR, EIS and ENM on corrosion monitoring

	LPR	EIS	ENM
Environments influence	No	Yes	Yes
Reference Electrode essential	Yes	Yes	No
Sample surface change	Yes	Yes	No
Easy data analysis	Yes	Yes	No
Result reproducible	Yes	Yes	No
Online data record	Yes	YES	Yes
Long term monitoring	No	No	Yes

6.2 Technical measures to avoid corrosion and lead deposition

6.2.1 Absorption of lead ions using steel slag

One of the options to avoid lead deposition in the geothermal installation is the absorption of lead ions on steel slag [5] [6]. The idea is to use the exchange reaction by depositing metalling lead on low grade steel in a filter unit directly after the production well. This way the lead ion concentration will be lowered and the risk on lead deposition in the geothermal installation will be minimized. After some time the steel slag with the lead deposit than needs to be discharged. Concentration of the deposits by absorption is at this moment not preferred, because of yet unknown and possibly high cost for the storage and/or reuse/disposal of the used adsorbent.

6.2.2 Cathodic protection

6.2.2.1 Passive cathodic protection

A common way of preventing steel corrosion in many applications (nautical) is the use of passive cathodic protection. In this case the steel is protected by putting it in an electrical contact with a very low noble material (for instance zinc).

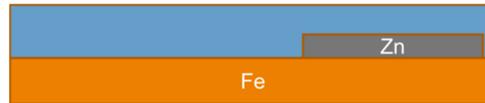


Figure 14: Schematic representation for the situation of passive cathodic protection

The as such formed galvanic element causes the zinc part to become more positively charged and thus to corrode while the open-circuit potential of the iron becomes more negative (cathodic) and thus prevents the iron from corrosion. Under "normal" water conditions this would cause the evolution of hydrogen due to the reduction of water at the iron/electrolyte interface.

However, in the case of a geothermal installation in the Slochteren reservoir, one has to bear in mind that the formation water also contains lead ions which can in this case also be reduced on the iron surface near the zinc piece, leading to unwanted deposition of metallic lead.

6.2.2.2 Active cathodic protection

An alternative way (Figure 15) of cathodic protection is to apply an external voltage between the iron substrate which we want to protect and a dimensional stable anode (DSA) placed close to the steel surface that needs to be protected.



Figure 15: Schematic presentation for protection of the installation using active cathodic protection

In this case, the oxidation reaction occurring at the DSA will be either the oxidation of water or the oxidation of the largely present chloride. Whether one or the other will take place largely depends on the choice of DSA material. Both of the oxidation products, oxygen and chlorine, will very likely cause corrosion problems in the installation further on the water stream.

Similar to the situation when using the passive cathodic protection it is very well possible that at the steel surface besides the reduction of protons/water also lead ions will be reduced.

6.2.2.3 Anodic protection

Figure 16 shows a schematic presentation for an active anodic protection using an external power supply and a dimensional stable cathode (DSK) which is placed in the electrolyte solution close to the steel surface that needs to be protected.

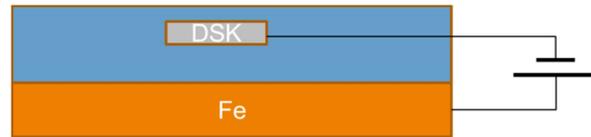


Figure 16: Schematic presentation when using active anodic protection

In this case the steel will act as the anode which therefore will oxidize. It will depend on the alloy composition and local pH at the steel/electrolyte surface how large a potential is needed to form a self-limiting passive oxide layer on the steel surface. Similar like in the case of cathodic protection again the cathode there will be the risk that besides the reduction of protons/water also lead ions will be reduced and thus metallic lead will be deposited.

6.2.3 Corrosion inhibitors

Three types of corrosion inhibitors are on the market:

Anodic inhibitors: usually act by forming a protective oxide film on the surface of the metal causing a large anodic shift of the corrosion potential. This shift forces the metallic surface into the passivation region. They are also sometimes referred to as passivators.

Cathodic inhibitors: act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface. The rates of the cathodic reactions can be reduced by the use of cathodic poisons. However cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking since hydrogen can also be absorbed by metal during aqueous corrosion or cathodic charging.

The corrosion rates can also be reduced by the use of oxygen scavengers that react with dissolved oxygen. Sulfite and bisulfite ions are examples of oxygen scavengers that can combine with oxygen to form sulfate.

Mixed inhibitors work by reducing both the cathodic and anodic reactions. They are typically film forming compounds that cause the formation of precipitates on the surface blocking both anodic and cathodic sites indirectly.

Evaluation of Corrosion inhibitors

Electrochemical methods are used routinely for the evaluation of the efficiency of corrosion inhibitors. The advantages of electrochemical methods are short measurement time and mechanistic information that they provide which help not only in the design of corrosion protection strategies but also in the design of new inhibitors.

The electrochemical measurements can be performed both in-situ as ex-situ using the similar set-up as is how on the left-hand side of Figure 13. When the measurement will be performed ex-situ than take care to use the appropriate conditions for the electrolyte with respect to the pH and the oxygen level (see paragraph 5.1.3). Using this, 3-electrode, set-up polarization curves (Figure 17 and

Figure 18) can be obtained from potentiodynamic current-potential curves which can be measured using the linear sweep method from a potentiostat. When the method is used in-situ, directly in the geothermal installation or in a loop, one can also monitor the use of the inhibitor in time.

A polarisation curve shows the on the material of interest measured current on a logarithmic scale as a function of the applied potential. Figure 17 and Figure 18 show two examples of the effect of a corrosion inhibitor on the polarisation curve for an anodic (Figure 17) and a cathodic (Figure 18) inhibitor.

In the example plot for the anodic inhibitor (Figure 17) it is shown that the open-circuit potential shifts to more positive potentials and that at more positive potentials a passivation plateau is observed which indicates that the inhibitor forms a blocking layer at the surface. Important is that the measured currents at potentials positive of the open-circuit potential when using the inhibitor are significantly lower than without the inhibitor (remember this is a logarithmic scale) indicating a much low corrosion current.

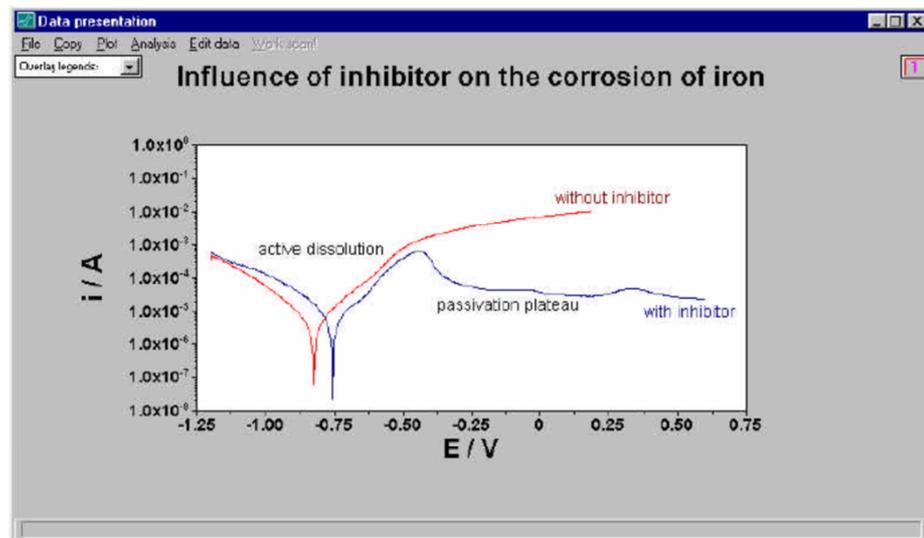


Figure 17: example of the influence of an anodic inhibitor on the polarisation curve. Red line is without inhibitor. Blue line with inhibitor.

The example in Figure 18 is for a cathodic inhibitor. In this case the open-circuit potential is shifted to more negative potentials upon adding the inhibitor to the electrolyte. Furthermore it can be observed that the anodic currents (at potentials positive of the open-circuit potential) are much smaller with the inhibitor indicating a much slower corrosion.

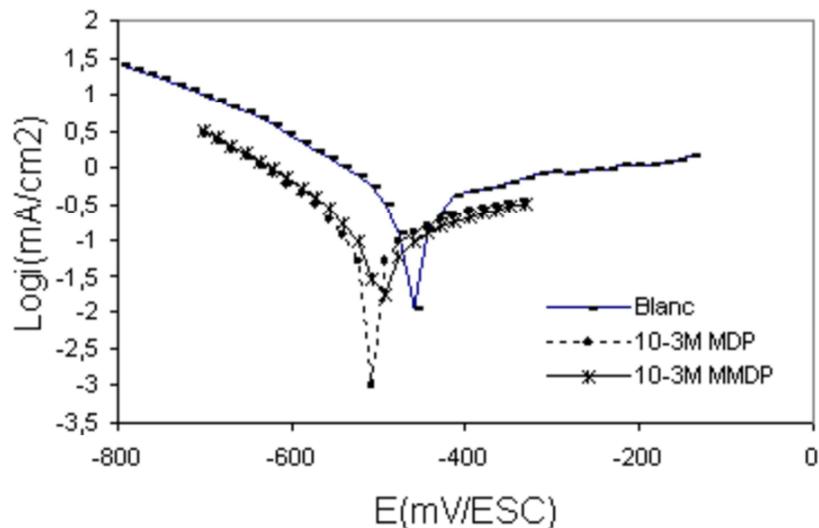


Figure 18: Example of the influence of an cathodic inhibitor on the polarisation curve. Blue line is without inhibitor. Black lines are with inhibitor.

Instead of using the polarisation method described above, which requires the use of a relatively expensive potentiostat, one can also use an LPR measurement (see paragraph 5.1.3). The LPR measurement however only measures in a small potential region around the open-circuit potential and only results in a corrosion resistance and sometimes the value of the open-circuit potential. This can however be enough for a first indication on the effect of the inhibitor.

6.2.4 *Materials selection and usage*

Below a brief overview will be given of the characteristics of different types of steel and alloys with respect to their corrosion behaviour.

Production and injection casing steel

Carbon steel:

- Contain less than 2.1% carbon in their chemical composition.
- Most commonly used, standard steel grades such as; K55, N/L80, P110
- K55 and N80 are the most basic steel grades with no additional corrosion resistant material present in their composition.
- L80 and P110 contain corrosion resistant material such as Manganese and Nickel, and undergo some form of heat treatment during the manufacturing phase.
- K55 grade carbon steel casing is often used as surface casing, while L80 is the most commonly used casing material in geothermal wells in the Netherlands under normal circumstances.
- Tubulars of this grade used as casing in geothermal wells can be vulnerable to corrosion depending on conditions like pH, temperature, oil content, CO₂ and TDS concentrations.

(super) Martensitic stainless / corrosion resistant steel:

- Contains at least 11.5% chromium such as Cr13 & Cr17 steel.
- Most onshore gas wells in the Netherlands use L80 casing but in offshore wells for casing and/or tubing also Cr13 is applied.
- Most wells in the Netherlands are completed with Cr13 tubing.
- Martensitic steels are not very corrosion resistant and are susceptible to sulphide stress cracking, which makes them ineffective in H₂S environments.
- On the other hand, they are extremely resistant to chloride stress cracking (CSC).
- Super martensitic stainless steel 316L: contains less carbon and more nickel and molybdenum, and is more resistant to corrosion than normal martensitic Cr13 steel.

Ferritic-austenitic steel alloy:

- Also known as duplex steel, this type of steel contains chromium, manganese, nickel, vanadium and molybdenum.
- It is much stronger than austenitic steel, and is also more resistant to corrosion pitting and stress cracking.
- The overall corrosion resistance is also better than that of regular austenitic steel.
- They are characterised by low carbon content, high chromium (at least 20%) and molybdenum content (3-5%), and low nickel content (less than 5%).
- Cr22 is the most frequently used duplex steel in the oil industry. Super duplex steel (Cr25) contains significantly more nickel and molybdenum. These type of materials are, due to their relatively high cost, usually only used in high demanding parts of the installation.

An overview of the major alloying components and the corrosion properties is given in Table 3 for many different installation materials used in geothermal installations. Besides the general corrosion resistance also the cracking resistance due to sulphide (SSC) and chloride (CSC) is shown.

Table 3: Corrosion properties of steel alloys

Some Prospective Alloys for Hot Well Tubulars						
Alloy	Major Alloying Constituents, wt%			General Corrosion Resistance ⁽¹⁾	Cracking Resistance	
	Cr	Ni	Mo		SSC	CSC
CrNi18-9	18-20	8-10.5	-	F	S	S
CrNiMo17-12-2	16-18	10-14	2-3	F	S	S
Cr13	11.5-13.5	0.75	-	S	S	R
Cr17	16-18	0.75	-	F	S	R
Super Cr13	11.5-13.5	5	2	F	F	R
Duplex SS (Cr 22)	22	5	3	G	S	G
Superduplex (Cr 25)	25	7	4	G	G	G
Incoloy 825	21.5	42	3	G	R	R
Inconel 625	21.5	min. 58	9	R	R	R
Inconel 625	22	26	5	G	R	R
Haynes 20 Mod	22	56	13	R	R	R
Hastelloy C-22	16	57	16	R	R	R
Hastelloy C-276	20	35	2.5	G	R	R
Carpenter 20 Cb						
SS = Stainless / Corrosion Resistant Steel				G = Good F = Fair S = Susceptible R = Resistant		

6.2.5 GRE/GRP pipes

A relatively novel approach to avoid unwanted electrochemical interactions with the installation materials is the use of non-conductive/isolating inner wall materials of the tubing. Glass Reinforced Plastic (GRP) pipes represent the ideal solution for the abduction of any kind of water, chemicals, affluent and sewers, because they combine the advantage of corrosion resistance, typical of plastics, with a mechanical strength which can be compared with the steel one.

Glass Reinforced Epoxy or GRE pipes are a valid alternative to carbon steel pipes especially for corrosive, aggressive and normal environments.

GRE pipe technology is based on high strength fiberglass (E-glass) and amine cured epoxy resin as basic material. Due to the use of plastics in GRP and epoxy in GRE one should carefully check if these materials are long term stable at the high down-hole temperatures.

The use of GRE and GRP pipes is still in the demo phase in some foreign geothermal installations and to our knowledge there is no experience with these innovative pipes for the Dutch geothermal installations.

6.2.6 How to prevent corrosion and lead deposition due to galvanic element formation

These measures refer to the lead deposition and corrosion due to the direct contact of two different type of two dissimilar materials in direct electrical and electrolytically contact as is described in sections 5.3 and 5.4.

In theory, galvanic corrosion can be prevented by avoiding the use of dissimilar metals in an assembly, by electrically separating the dissimilar metals with an insulating material or by physically insulating the environment from the metal

surface with a coating impermeable to water. In reality, however, complete prevention is often not possible, as various metals are needed in the installation and an absolute coating is only obtained in theory. Therefore measures need to be taken to minimize the possibility and extent of galvanic corrosion and/or lead deposition.

Some common practical approaches are as follows Zhang [7]:

- Avoid combinations of dissimilar metals that are far apart in the galvanic series applicable to the environment.
- Avoid situations with small anodes and large cathodes.
- Isolate the coupled metals from each other. Be aware that spacers which are perfectly isolating at the start might crack or change composition during usage and start to conduct in time.
- Also be aware when making ground connections to the installation to avoid direct contact between two dissimilar materials through a direct connection via the grounding cables.
- Reduce the aggressiveness of the environment by adding inhibitors (this is discussed in section 6.2.3)
- Use cathodic protection of the bimetallic couple with a rectifier or a sacrificial anode. (this will be discussed on further in section 6.2.2)
- Increase the length of solution path between the two metals. This method is beneficial only in electrolytes of low conductivity, such as freshwaters, because strong galvanic action exists several meters away in highly conductive media, such as seawater. This measure will therefore not be effective in the very high conductive water of geothermal installations.

The use of these approaches must meet the specific requirements of each application. Sometimes one is sufficient, but a combination of two or more may be required in other situations. It must be emphasized that the most effective and efficient way to prevent or minimize galvanic corrosion and the accompanying lead deposition is to take measures early in the design stage of the geothermal installation.

7 Conclusions / recommendations

Based on a theoretical approach using Pourbaix diagrams and the Nernst equation to determine the relevant equilibrium potentials, the electrochemical reactive species are determined for the water composition of the Slochteren reservoir. It is shown that there is a relatively low impact of temperature on the calculated redox potentials. The main electroactive species are protons (obtained by the dissolution of carbon dioxide in water), Cu, Ni and Lead. Since the Cu and Ni concentration in the formation water is low it is not expected to have a great impact as is also observed in practice. The at least 100 times higher concentration of lead in the formation water gives rise to the deposition of lead on the inner surfaces of the installation.

Two types of mechanisms for lead deposition are described: lead deposition due to an exchange with the less noble iron from the steel casings and lead deposition due to galvanic element formation when two different types of installation material are used in direct electrical contact with each other. In both cases lead deposition is accompanied by the corrosion of steel.

Based on the corrosion and lead deposition mechanisms monitoring tools and preventive measures such as inhibitors, material selection and prevention of galvanic element formation are described.

8 Signature

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