Possible effects of external electrical fields on the corrosion of copper in bentonite

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Summary

External potentials that develop across a repository may interact with the copper canister. A study was undertaken to investigate the potential corrosion effects of voltage differences in a repository.

A set of experiments was performed to study the tendency of copper in bentonite to corrode under influence of an externally applied electrical field. A model study was made to estimate possible corrosion effects of an external electrical field on a full-scale canister in the KBS-3 concept. The interaction between the repository represented by a copper canister in bentonite, and an external electrical field is illustrated with an example.
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1 Background

Electric current in groundwater and in bentonite consists of charge, transported as ions. In order to interact with a metallic structure, electrode reactions must take place. At the point where the current enters the metallic structure there is a reduction process and the point where current leaves the metal there is an oxidation process. One of the oxidation processes may be oxidation of the metal itself, which leads to corrosion. The rate of these electrode processes is strongly dependent on the voltage across the metallic structure. To a first approximation there is a linear dependence between the potential and the reaction rate. This linear dependence holds for the reduction at points where current enters to metal and for the oxidation at points where current leaves the metal. It should be mention that linear dependence between rate and electrochemical potential is not general. However, for small disturbances of up to 50 mV around the undisturbed state, the linear approximation is useful.

The reaction rate of an electrode reaction is often described as a current density with the SI-units (A/m²). The linear dependence is therefore often referred to as a resistance with the SI-units (Ω m²). In electrochemistry and corrosion science, the term polarisation resistance, \( R_p \), is used to describe the linear portions of the dependence of current on potential.

The polarisation resistance of copper in bentonite is thus a parameter that describes the corrosion effects of external electrical fields in a repository. However, the polarisation resistance responds to all electroactive species in the system and the conservative assumption made here is that corrosion of copper is the only possible oxidation.
2 Experimental

Canister copper was obtained from SKB and presaturated bentonite was obtained from Clay Technology. The bentonite samples come from an experiment at Åspö HRL and may be considered to be saturated with ground water.

Copper was machined to small discs similar to coins in shape and size, 32 mm diameter and ~1 mm thick (~17 cm² area). Copper wires were attached in small holes drilled into the edges of the discs. Bentonite was machined to cylindrical discs (70 mm diameter and ~10 mm thick) with disc shaped cavities for the copper discs and grooves for the wires. Four copper discs and five bentonite cylinders were used in each experiment. The upper end bentonite cylinder was about 30 mm thick.

The polarisation resistance reflects the rate of electrochemical reactions. In order to obtain values that are relevant for oxygen free conditions it is necessary to exclude oxygen from the system under study. The equipment was therefore assembled in a glove box. The bentonite surfaces were wetted with deionized water before the bentonite-copper staple was assembled.

The staple of copper discs and bentonite cylinders were packet into a plastic tube and this tube was put into a stainless steel cylinder. Deionized water was flushed over and inside the plastic tube. Steel rods and nuts allowed the flanges of steel cylinder to be screwed tightly before the bentonite could generate its full swelling pressure. For the electrochemical measurements, the whole steel cylinder had to be removed from the glove box. The steel cylinder was then immersed in deionised water in a large desiccator. The gas volume above the water surface was continuously purged with nitrogen gas.

Figure 2-1 shows a schematic drawing of the four copper discs enclosed in bentonite. An AC signal of varying frequency applied to the outer two copper discs generates an electrical field for the inner two copper discs. The current induced between the inner two copper discs is measured by Zero Resistance Ampere meter (ZRA). Signals proportional to the currents I1 and I2 are fed to a Frequency Response Analyser for determination of the relative amplitude and phase angle.

**Figure 2-1.** Schematic illustration of the four copper discs in bentonite in the experiments. The illustration shows how the two outer discs were used to generate an electrical field. This field causes a part of the current to flow between the two inner discs.
Several types of measurements were performed in order to determine the polarisation resistance of copper in bentonite. Measurements were complicated because of slow drift in potentials when the current was controlled and slow drift in current when the potential was controlled. Frequency response analysis confirms that the system is characterised by very high time constants.

The Bode plot in Figure 2-4 shows results from an experiment where the copper discs were connected as in Figure 2-1. The two currents, \( I_1 \) and \( I_2 \) are fed into a frequency response analyser. The ratio between the two currents is analysed in phase and modulus for various frequencies of the AC signal.

Figure 2-4 shows that at frequencies above 10 Hz, a large fraction of the current between the two outer copper discs also passes the two inner copper discs. At low frequencies almost the whole current stays in the bentonite and only a small percentage passes the inner copper disc couple. Unfortunately, no low frequency limit for the ratio can be discerned from Figure 2-4. Frequencies lower than 0.01 Hz were not measurable. The very small amplitude of the current between the two inner copper discs made accurate measurements impossible. The polarisation resistance can therefore not be measured by AC technique.
Galvanostatic polarisation between two copper discs was selected for the determination of the polarisation resistance for direct current. A constant current of 100 nA was passed between the discs giving a current density of about 5.9 nA/cm². The voltage between the two discs was monitored for several days and seemed to level out at about 365 mV. The polarisation resistance is calculated as

\[ \frac{365 \times 10^{-3}}{5.9 \times 10^{-9} / 2} = 3.1 \times 10^7 \text{ W cm}^2 = 3,100 \text{ W m}^2 \]

Figure 2-4. Bode plot for the ratio between the currents I₂ and I₁ in Figure 1-1.

Figure 2-5 shows the potential between two copper discs when 100 nA was passed between them for several days. What appear as sharp jumps in the potential are caused by pauses in the registration while maintaining the polarisation.

Figure 2-5. Potential difference between two copper discs when a constant current density of 5.9 nA/cm² is passed between them.
3 Model studies

Commercial software, Comsol multiphysics, was used to calculate the possible corrosion effects of an external electrical field on a full-scale canister in the KBS-3 concept. In addition to the polarisation resistance, the conductivity of bentonite is necessary. A value for MX-80 with a water contents of 15–20% (Åspö ground water) was used (Miehe et al. 2000). A resistivity of about 2 Ω m is reported for these conditions.

The model conditions are illustrated in Figure 3-1. It is assumed that there is an external field that generates a certain external voltage between the top and bottom of the cylinder, let's say 1 mV. Symmetry causes the copper canister to attain a potential of exactly half of that value (0.5 mV).

In order to simplify the FEM-calculations only a fraction of the canister and bentonite was considered. Symmetry implies that the upper half is a mirror image of the lower half. Figure 3-2 shows the part of the bentonite that was used in the calculations. The colours indicate the local potentials in the bentonite.

Figure 3-3 shows a plot of the function \((0.5-V)/R_p\) where \(V\) is the local potential in the bentonite and \(R_p\) is the polarisation resistance of copper. This function is significant only at the bentonite/copper boundary and there \((0.5-V)/R_p\) represents the local current density from the copper to the bentonite, i.e. the corrosion current. Figure 3-3 shows that the current is close to zero at the middle of the canister and that the current density has the highest values at the end of the canister. The highest current density is about \(1.6 \times 10^{-4}\) mA/m². The total current through the bentonite is about 0.14 mA, when the whole cross section is included.

The corrosion depth as a function of time was estimated as:

\[
\text{penetration rate} = \frac{i \cdot M_{W_{Cu}}}{F \cdot \rho} \left( \frac{A/m^2 \cdot kg/mole}{As/mole \cdot kg/m^2} = m/s \right)
\]

Where \(i\) is the current density \(= 1.6 \times 10^{-7}\) A/m² (1 mV across the bentonite)

\(M_{W_{Cu}}\) is the molar weight of copper \(= 63.546 \times 10^{-3}\) kg/mole

\(F\) is Faraday’s constant \(= 96,485\) As/mole

\(\rho\) is the density of metallic copper \(= 8.92 \times 10^{3}\) kg/m³

The corrosion depths that come out of this calculation is listed in Table 3-1 below.

When considering the likelihood that external electrical fields can generate potential differences across the bentonite, it should be realised that the bentonite has a tendency to short-circuit the external electrical field, locally. For a potential difference of 1 mV to arise, as in the calculations above, about 0.14 mA must be drawn from the external field.

### Table 3-1. Calculated corrosion depths for various times of exposure to an external electrical field of 1 mV across the bentonite in a repository.

<table>
<thead>
<tr>
<th>Corrosion depths as function of time</th>
<th>1.18×10⁻¹⁷ m/s</th>
<th>1.18×10⁻¹¹ μm/s</th>
<th>0.00037 μm/year</th>
<th>0.37 μm /1,000 year</th>
<th>37 μm /100,000 years</th>
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<tbody>
<tr>
<td>1.18×10⁻¹⁷ m/s</td>
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<td>1.18×10⁻¹¹ μm/s</td>
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<td>37 μm /100,000 years</td>
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</table>
Figure 3-1. Model conditions. A bentonite cylinder with a cavity for the copper canister. Outer diameter 1.75 m, inner diameter 1.05 m. The wall thickness is 35 cm everywhere. An external field generates certain external voltage between the top and bottom of the cylinder. Symmetry causes the copper canister to attain a potential of exactly half of that value (0.5 mV). (The potential distribution above refers to the bentonite without the copper canister).
**Figure 3-2.** Potential distribution in the bentonite from the model conditions. With the copper cylinder present at a uniform potential of 0.5 mV. Polarisation resistance 3,100 $\Omega$ m$^2$. 
Figure 3-3. Plot of the function \((0.5-V)/Rp\) where \(V\) is the local potential in the bentonite and \(Rp\) is the polarisation resistance of copper. \((0.5-V)/Rp\) is the local current density for corrosion under the model conditions.
# 4 Properties of an external electrical field

In borehole KFM04 at the Forsmark site, a potential difference of about 2.5 V has been observed between the upper and lower levels of the borehole. There are anecdotal observations of a voltage difference of up to 5 V with a current of 10 mA passing when the upper and lower levels of the borehole are short-circuited.

Electrical fields of this magnitude should of course not be present at the site of a repository. But, let us anyway try to estimate the corrosion effects of a situation where the canister is located in an external field with the properties described: $E_{\text{max}} = 5.0$ V, $I_{\text{max}} = 10$ mA.

An equivalent circuit for this field is shown in Figure 4-1.

The value of the internal resistance $R_i$ is calculated from the maximum current observed, $R_i = 5V/10$ mA $= 500 \ \Omega$. The resistance of the repository is estimated from the model calculations: $R(\text{repository}) = 1mV/0.14mA \sim 7 \ \Omega$. The resulting voltage across the repository would be: $5V/7/(7+500) \sim 70$ mV. The polarisation resistance for the copper/bentonite interface is linear over this potential region and the corrosion effect is proportional to the current. The maximum depth of corrosion is thus 70 times the values in Table 3-1.

An external field with 5V maximum voltage and an internal resistance of 500 $\Omega$ would give a corrosion attack of about 2,600 $\mu$m in 100,000 years.

![Figure 4-1. Sketch of an external electrical field with a voltage of 5V and an internal resistance, $R_i$.](image-url)
References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.se/publications.