An electrochemical impedance spectroscopy study of copper in a bentonite/saline groundwater environment

Bo Rosborg *, Jinshan Pan

Royal Institute of Technology, Div. Corrosion Science, Drottning Kristinas väg 51, SE-100 44 Stockholm, Sweden

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**Abstract**

Pure copper samples have been exposed for 6 years in a bentonite test parcel in the Äspö Hard Rock Laboratory, which offers a realistic environment for the conditions that will prevail in a deep repository for high-level radioactive waste disposal in Sweden. After retrieval of the test parcel, a bentonite test package containing the samples was placed in a container and sealed with a thick layer of paraffin, and later on new copper and platinum samples were installed. An electrochemical impedance spectroscopy study has been performed on the pre-exposed and new copper samples for different durations in the retrieved test package.

The impedance spectra for copper in the bentonite/saline groundwater environment change considerably with time of exposure. The change is more pronounced at higher than at lower frequencies. It is presumed that the corrosion resistance of pure copper in this environment mainly depends on a thin protective cuprite film that forms readily, and on a thick porous outer corrosion product layer (mainly cuprite) that develops slowly and partly intermixes with the bentonite. The impedance data revealed that both the inner and the outer corrosion product layer were involved in the impairment and the recovery of the corrosion resistance when the copper interface was disturbed during retrieval of the bentonite test package.

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1. **Background**

The principal strategy for high-level radioactive waste disposal in Sweden is to enclose the spent nuclear fuel in tightly sealed copper canisters that are embedded in bentonite clay about 500 m down in the Swedish bed-rock (Fig. 1) [1]. The repository will be built by materials that occur naturally in the earth’s crust. The idea is that the repository should imitate nature as closely as possible.

"Nature" has proven (i) that copper can last many million of years under proper conditions—native copper has been preserved for nearly 200 million years in an environment which is similar to the repository near-field environment [2], (ii) that bentonite clay has existed for many million years—Wyoming bentonite clay for instance was formed during Cretaceous, i.e. more than 65 million years ago [3], and (iii) that the Fennoscandia bedrock shield is stable—the bedrock of interest was formed during the Precambrian period, i.e. more than 545 million years ago [4].

Besides rock movement, the biggest threat to the copper canister in the repository is corrosion. It is believed that copper will last if proper environmental conditions are established and maintained [5]. The most important task from a corrosion point of view is to ascertain a proper near-field environment for the copper canister. This electrochemical impedance spectroscopy study of copper in a bentonite/saline groundwater environment has been performed to gain information about the corrosion behaviour of copper in such environments.

2. **The material–environment system**

Here information about the copper material, the saline groundwater, the bentonite clay, and the near-field environment is presented with the dual purpose of describing the anticipated conditions in a deep repository for high-level radioactive waste disposal in Sweden, and the actual test conditions for the copper samples used in the present study.

Cylindrical electrodes and rectangular coupons of copper have been exposed for 6 years in a bentonite test parcel at a depth of 450 m in the Äspö Hard Rock Laboratory (Fig. 2a) [6]. The laboratory offers a realistic environment for different experiments and tests under the conditions that will prevail in a deep repository.
Groundwater in granitic rock in Sweden is oxygen-free and reducing below a depth of 100–200 m. The redox potential below this depth ranges between −200 and −350 mV SHE and the water has a pH ranging from neutral to mildly alkaline (pH 7–9) [5,7,8]. The chloride concentration in the groundwater can vary within very wide limits, ranging from 5 mg/dm³ to 50 g/dm³. Groundwater analyses from different parts of Sweden show sulphide concentrations ranging from <0.01 up to 1 mg/dm³, with 0.1 mg/dm³ as a typical value. Dissolving sulphide minerals are one source of sulphide in the groundwater, but sulphide will also be produced by a specific group of micro organisms, the sulphate-reducing bacteria, which are common in deep groundwater [9].

Table 1 shows the composition of the groundwater at the test position in the Åspö Hard Rock Laboratory.

2.3. The bentonite clay

The main mineral constituent in bentonite clay is montmorillonite, which has a sheet like crystal structure [3]. As an example, Wyoming bentonite used in this study and sold under the commercial name MX-80 is dominated by natural sodium montmorillonite clay (~75% by weight), which is responsible for the desired physical properties. The remaining part consists of quartz (~15%), feldspars (~7%), carbonates (~1.4%), sulphides (~0.3%), and organic carbon (~0.4%). The mean mineralogical composition of the montmorillonite part is given by

\[ (\text{Al}_{1.5}\cdot \text{Fe}^{2+}\cdot \text{Fe}^{3+}\cdot \text{Mg}_{0.48}) (\text{Si}_{1.12}\cdot \text{Al}_{0.88}) \quad \text{O}_2\text{(OH)}_4 \quad \text{Na}_{0.46}\text{Ca}_{0.06}\text{Mg}_{0.52}\]

The cation exchange capacity is around 0.8 eq/kg bulk. The natural exchangeable cations are sodium (~85%), calcium (~10%), magnesium (~4%) and small amounts of potassium (~0.3%). The specific surface area is around 550 m²/g material and the grain density is around 2750 kg/m³.

The target density for LOT test parcel A2 at full water saturation was 2000 kg/m³. The actual values fall in the range 1900–2000 kg/m³ [6].

2.4. The near-field environment

Initially, a limited amount of air will be left in a repository and a bentonite test parcel after emplacement, which during the water saturation phase partly will be trapped by the low permeability rim of groundwater-saturated bentonite [5]. After water saturation the chemical environment in the immediate vicinity of the copper surface is determined by the composition of the bentonite pore water. This is, in turn, determined by the interaction between the bentonite and the saline groundwater in the surrounding rock. The entrapped oxygen will be consumed through reactions with minerals in the rock and the bentonite, through copper corrosion, and also through microbial activity.

After the oxygen has been consumed, corrosion will be controlled completely by the supply of dissolved sulphide to the copper surface. However, this anoxic period is beyond the scope of the present study which concerns the oxic period.

3. Experimental

After retrieval of the test parcel shown in Fig. 2b, a bentonite test package containing the cylindrical copper electrodes was first furnished with a copper sheet on the outside (to be used as a counter electrode) and then placed in a plastic container, equipped with two reference electrodes, and sealed with a thick layer of paraffin to maintain a similar environment. Later on new copper and platinum electrodes were installed in the test package. Electrochemical impedance measurements were performed on both the pre-exposed and the new copper electrodes for different durations after retrieval and lengths of exposure. Platinum electrodes were included to obtain information about the electrolytic properties of the bentonite/saline groundwater environment. All measurements were performed at room temperature.

3.1. Retrieval of test package with pre-exposed copper electrodes

Fig. 3 shows how the test parcel was retrieved from the Åspö Hard Rock Laboratory, how the bentonite test package containing the copper electrodes was cut off from the test parcel after removal of the surrounding rock, and how the bentonite test package was scaled with a thick layer of paraffin (on all sides).
Fig. 2. (a) View of the Åspö Hard Rock Laboratory above and below ground and (b) the bentonite test parcel (LOT A2) exposed for 6 years in the laboratory. The cylindrical copper electrodes were positioned in bentonite ring 36 (24°C) and the copper coupons in bentonite rings 22 (75°C) and 30 (30°C).

When the copper sheet was placed on the outside of the bentonite test package next to the pre-exposed copper electrodes in bentonite ring 36, the bentonite was first wetted with Åspö groundwater (Table 1). Then the external copper sheet was tied to the test package.

Two standard reference electrodes (for the purpose of verification) were installed in the bentonite test package just before covering the top of the test package with paraffin. Holes were drilled into the bentonite at two locations opposite to one another, a tube of Perspex with a ceramic frit in the bottom end was placed in each hole, some Åspö groundwater was poured into the tube, and the reference electrode was placed in the tube. On several occasions after retrieval of the test package additional Åspö groundwater has been added in order to re-establish a proper liquid junction. The reference electrodes have also been exchanged. No attempts have been made to deaerate the groundwater before it was added.

The three pre-exposed Ø30 mm × 90 mm copper electrodes in bentonite ring 36 (electrode area 98.7 cm²) are positioned vertically in a row 1 cm apart and with each electrode 10 cm from the centre of the ring. The reason for using cylindrical electrodes was to facilitate installation.

The real-time corrosion monitoring before and after retrieval of the bentonite test package has been performed with a SmartCET®1 corrosion monitoring system and three-electrode configurations [10]. In short, polarization resistance and harmonic distortion analysis techniques are used to derive information regarding the general corrosion rate. A voltage perturbation with a frequency of 0.01 Hz and 50 mV peak-to-peak amplitude is applied and the current response is measured and analyzed synchronously with the perturbing sine wave. The harmonic distortion analysis involves the measurement of the higher harmonic content at 0.02 and 0.03 Hz, which then allows for estimates of the anodic and cathodic Tafel slopes and the Stern–Geary coefficient. The applicability and accuracy of the obtained data has earlier been discussed [11].

It is obvious from the real-time corrosion monitoring results shown in Fig. 4 that the pre-exposed copper electrodes were greatly disturbed during retrieval of the test parcel, which caused a major

Table 1
The actual groundwater composition from the Åspö Hard Rock Laboratory

<table>
<thead>
<tr>
<th>Ion</th>
<th>mM</th>
<th>mg/dm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>91</td>
<td>2100</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.2</td>
<td>8</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>47</td>
<td>1890</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.8</td>
<td>42</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>181</td>
<td>6410</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.2</td>
<td>10</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>5.8</td>
<td>560</td>
</tr>
<tr>
<td>HS⁻</td>
<td>0.005</td>
<td>0.15</td>
</tr>
<tr>
<td>pH 7.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{\text{red}}$ - 308 mV SHE</td>
<td></td>
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</tr>
</tbody>
</table>
change in the recorded corrosion rate (compare Fig. 4a and b) and the corrosion potential to change considerably after retrieval (Fig. 4c). During the retrieval procedure the copper electrodes experienced mechanical disturbances from a decreased bentonite swelling pressure, drilling and cutting operations, and a temperature excursion of about 10°C [6].

After retrieval the conditions for the pre-exposed copper electrodes in the bentonite test package are anticipated to be quite similar but of course not the very same as before, since the pressure on the bentonite test parcel in the rock has been released. The paraffin layer has also been partly opened several times.

3.2. Installation of new copper and platinum electrodes

After a period of measurements with the pre-exposed copper electrodes only, three new Ø10 mm × 50 mm copper electrodes (electrode area 16.5 cm²) were installed in the bentonite test package. Part of the paraffin layer was removed, three holes were drilled into the bentonite in a triangular configuration 1 cm apart, each hole was soaked with Aspö groundwater for a short period, an electrode was placed in the hole, and finally the hole was back-filled with bentonite borings and sealed again by paraffin.

Later on one Ø5 mm × 25 mm copper and three Ø5 mm × 25 mm platinum electrodes (electrode area 4.32 cm²) were installed simi-

![Fig. 3. Retrieval of the pre-exposed copper electrodes in January 2006. (a and b) Lift-up of the test parcel with surrounding rock, (c and d) cutting off the bentonite test package after removal of surrounding rock, and (e and f) moulding the bentonite test package in paraffin.](image)

![Fig. 4. The recorded corrosion rate: (a) just before retrieval and (b) after retrieval, and (c) the corrosion potential of one of the pre-exposed copper electrodes after retrieval. (Time on the x-axis is given as yy-mm-dd.)](image)
The positions of the new copper and platinum electrodes in the bentonite test package. (The Ø10 mm × 50 mm copper electrodes to the upper left and the Ø5 mm × 25 mm copper and platinum electrodes to the lower left in the figure.)

Fig. 5. The positions of the new copper and platinum electrodes in the bentonite test package. (The Ø10 mm × 50 mm copper electrodes to the upper left and the Ø5 mm × 25 mm copper and platinum electrodes to the lower left in the figure.)

larly. The platinum electrodes were positioned 3, 4 and 5 cm apart in a right-angled triangle configuration. The copper electrode was placed half-way between the two platinum electrodes that are 4 cm apart.

Fig. 5 shows the positions of the new copper and platinum electrodes in the bentonite test package, and Fig. 6 shows the recorded corrosion rate and the corrosion potential of one of the Ø10 mm × 50 mm copper electrodes after installation. Quite similar corrosion rates and corrosion potentials have been established for the pre-exposed and new copper electrodes after long exposures (compare Figs. 4 and 6).

3.3. Impedance measurements

A Solartron Analytical 1287 Electrochemical Interface in combination with a 1250 Frequency Response Analyzer, controlled with the ZPlot software, was used for the three-electrode electrochemical impedance measurements. Strictly, the measurements were performed under potentiostatic control, as the working electrode potential was locked to its open circuit potential at the start of the measurement. However, the material–environment system shows such stability that the measurements can be considered performed during free corrosion. A saturated calomel electrode was used as reference and either the external copper sheet (electrode area >1 dm²) or one of the cylindrical platinum electrodes (electrode area 4.32 cm²) as counter electrode. The applied voltage amplitude was 5 mV rms and seven data points per decade were recorded.

3.4. Supporting information from exposed copper coupons

Since measurements on the cylindrical copper and platinum electrodes in the retrieved test package are still running, post-test examination has so far only been performed on the copper coupons (dimensions 60 mm × 15 mm × 1.5 mm). After 6 years exposure in the bentonite/saline groundwater environment at Åspö the copper coupons revealed that a brownish corrosion product layer with blue-green corrosion products here and there on top of it covered most of the surface [6]. Fig. 7 shows the appearance of a copper coupon immediately after breaking apart the bentonite piece containing the coupon. Corrosion products can also be seen on the bentonite surface facing the copper coupon, thus revealing a better adherence to the bentonite on part of the surface.

Energy dispersive X-ray spectroscopy in a scanning electron microscope revealed higher Al, Si and Fe contents in the blue-green corrosion products, as compared to the adjacent surface on a coupon, showing that the blue-green corrosion products penetrated into the bentonite.

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Fig. 6. The recorded corrosion rate and the corrosion potential of one of the new Ø10 mm × 50 mm copper electrodes after installation. (Time on the x-axis is given as yy-mm-dd.)

Fig. 7. Appearance of a copper coupon after 6 years exposure in the bentonite/saline groundwater environment at Åspö. (Do observe corrosion products also on the bentonite surface facing the copper coupon after breaking apart the bentonite piece.)

○ From Scribner Associates Inc., 150 East Connecticut Avenue, Southern Pines, NC 28387, USA.
X-ray diffraction measurements were performed on corrosion product scrapings using a Guiner–Hägg powder diffraction camera (wave length Cu Kα, 1.54060 Å). The evaluation procedure involved comparing the obtained spectra with an average spectrum for bentonite from the very same test parcel (bentonite ring 33), since bentonite was anticipated to be present in the scrapings, and with reference spectra for different copper corrosion products. The X-ray diffraction measurements have confirmed that the main constituent of the brownish corrosion product layer is cuprite, Cu₂O, and that the blue-green corrosion products are paratacamite, Cu₂(OH)₃Cl [12].

The average corrosion rate of copper based on weight measurements of the copper coupons was found to be less than 0.5 µm/year. This is lower than the recorded values from the real-time corrosion monitoring of the pre-exposed copper electrodes by means of polarization resistance and harmonic distortion analysis methods before and after retrieval (Figs. 4a and b). Possible reasons for overestimation of the corrosion rate by these methods were discussed previously [11,13]. One evident reason is that the corrosion rate is merely overestimated by not using a sufficiently low measuring frequency (0.01 Hz) to obtain the true polarization resistance.

4. Results and discussion

The corrosion behaviour of the copper electrodes in the bentonite test package is governed by the composition of the bentonite pore water next to the copper surface; this has, in turn, been determined by the interaction between the bentonite and the saline groundwater during 6 years exposure in the Åspö Hard Rock Laboratory (Table 1). For the present oxic conditions the dominating corrosion stimulating species are chloride and oxygen.

The corrosion behaviour of copper in chloride media has been extensively treated in two recent reviews [5,14]. Most of the available data, however, refers to short test duration for obvious reasons. Few studies concern long-term exposure and repository environments. Any electrochemical impedance spectroscopy study of copper in a near-field environment involving long-term exposure has not been found in the open literature.

Before showing the impedance spectra for copper after different test durations, impedance spectra for platinum in the bentonite/saline groundwater environment will be presented, to gain some information about the electrolytic properties of the bentonite saturated with saline groundwater.

4.1. Platinum electrodes

Fig. 8 shows the impedance spectra for the three platinum electrodes exposed in the bentonite test package for 3 days. The measurements were performed with different electrode configurations: one platinum electrode acting as working electrode and another as counter electrode, i.e. in total six combinations. The results reveal a satisfactory reproducibility. The electrolyte resistance is fairly low, as seen from the impedance modulus value in the high frequency range (frequency-independent). In this case a simple equivalent circuit (that is circuit A in Fig. 9) consisting of a polarization resistance $R_p$ and an interfacial capacitance in parallel, connected in series with the electrolyte resistance $R_e$, can be satisfactorily used for spectrum fitting. A constant-phase element (CPE) was used instead of a pure capacitance to account for a non-ideal capacitive response of the interface. The impedance function of the CPE is represented by $Z_{CPE} = \frac{1}{Q(jω)^n}$, where $Q$ is the constant corresponding to the interfacial capacitance, $j$ is the imaginary number, $ω$ is the angular frequency, and $n$ is an exponential factor in the range between 0 and 1 [15]. A value of 1 describes an ideal capacitor and a value of 0 describes an ideal resistor. Examples are given in Ref. [16]. The spectrum fitting using the ZView software gave a $R_p$-value of 75 ohm cm$^2$, a $Q$-value of 6.3 × 10$^{-5}$ s$^n$/ohm cm$^2$, a $n$-value of 0.91, and a $R_p$-value of 1.7 × 10$^6$ ohm cm$^2$.

It has been reported that the impedance response of bentonite is influenced by its water and salt contents [17]. The electrolyte resistance and interfacial capacitance values (roughly $Q$) obtained for the platinum electrodes in this study indicate that the bentonite saturated with the saline groundwater behaves like an aqueous electrolyte with a high ionic mobility.

4.2. New copper electrodes

Fig. 10 shows the impedance spectra for new copper electrodes exposed in the very same bentonite test package for 3 days and for 5 months. The corrosion potentials were 90 and 179 mV SHE, respectively.

The spectrum for copper after 3 days exposure is dominated by one relaxation (time constant). Following the same procedure as above, the spectrum fitting to the simple circuit A in Fig. 9 gave a $R_p$-value of 57 ohm cm$^2$, a $Q$-value of 4.9 × 10$^{-4}$ s$^n$/ohm cm$^2$, a $n$-value of 0.80, and a $R_p$-value of 4.5 × 10$^5$ ohm cm$^2$. (The slightly lower $R_p$-value compared to that for platinum above is a result of the electrode configuration.) As judged from the $Q$-values the interfacial capacitance for copper after 3 days exposure is significantly higher compared to platinum. There are ample evidences that a thin protective cuprite film forms on copper in aerated aqueous solutions at neutral pH [18–21]. In the presence of chloride the film is relatively rough and exhibits a higher capacitance as found from electrochemical impedance measurements.

However, equivalent circuit A is too simple to fully describe the present data. In several studies of copper in chloride solutions two

\footnote{Denoted $R_p$ in Fig. 9.}

\footnote{From Scribner Associates Inc.}
or three time constants have been observed and different equivalent circuits used for data fitting [e.g. 22, 23]. Equivalent circuits B and C in Fig. 9 are generally used for impedance spectra fitting for copper exposed to saline solutions and mathematically very good fits can be obtained [22]. The spectrum for copper after 3 days exposure shows good fits to either one of the equivalent circuits B and C in Fig. 9. The fit to equivalent circuit B is shown in Fig. 10. Different interpretations of circuit elements exist and are briefly discussed in Ref. [22]. In short, however, there is presently no consensus how to unambiguously interpret the different parameters obtained from spectra fitting and decide upon which physical model match the best. Impedance data on its own is not enough, but need support from micro structural and surface analysis information. Since the post-test examination of the electrodes in the present study is yet to be done, a thorough evaluation of the impedance data will be performed later, and the interpretation is focused on the main features of the spectra.

The spectrum for copper after 5 months exposure shows mathematically a good fit to equivalent circuit C, see Fig. 10. The peaks in the phase angle were greatly decreased as compared to the results from the 3 days exposure, which indicates that the surface film becomes quite heterogeneous. This prohibits spectra fitting by using a simple equivalent circuit. The shape (two time constants feature) of the impedance spectrum indicates that a bi-layer corrosion product film has been formed on the copper surface, which is well known for copper and copper alloys in different systems [18–21]. In this study, it is presumed that a thick porous corrosion product layer (mainly cuprite, and possibly other compounds) is formed on top of the thin protective cuprite film.

Compared to copper after 3 days exposure, the impedance modulus for copper after 5 months exposure has increased both in the high and the low frequency region. The large increase of the impedance modulus (frequency-dependent) in the high frequency range is interpreted as due to the development of the outer porous corrosion product layer. It appears that this porous layer contribute to a quite high corrosion resistance. For a layer with open pores filled with a strong electrolyte (e.g. anodised aluminium), the high frequency impedance represents mainly the electrolyte resistance (depending on the ionic mobility of the electrolyte) and should
Fig. 12. (a) Presumed evolution of the interface for the new copper electrodes during exposure in the retrieved bentonite test package. (b) Presumed evolution of the interface for the old pre-exposed copper electrodes during exposure in the retrieved bentonite test package.

remain relatively constant during exposure [24]. In this study, however, the development of the outer porous corrosion product layer seems to result in a decreased ionic mobility of the electrolyte, i.e. the bentonite saturated with saline groundwater. It may be speculated that some ion exchange process occurs at the interface, which results in an interplay of the copper corrosion products and the surrounding bentonite after a prolonged exposure.

4.3. Pre-exposed copper electrodes after retrieval

Fig. 11 displays the impedance spectra for one of the pre-exposed copper electrodes for different durations after retrieval. Mathematically good fits of the data are obtained to equivalent circuit C in Fig. 9. The corrosion potentials and recorded corrosion rates are given in the figure caption. It is obvious that the impedance spectra change considerably with time, and that the change is more pronounced at higher than at lower frequencies (more than two orders of magnitude difference above 10 Hz compared to less than one below 0.01 Hz). The main features of the spectra suggest a bi-layer corrosion product film on the copper surface.

Compared to the new Ø10 mm × 50 mm copper electrode after 5 months exposure, the spectrum obtained for the pre-exposed copper electrode 2 weeks after retrieval shows lower impedance both in the high and in the low frequency range. This was obviously caused by the retrieval procedure (see above). For a continued exposure the impedance increased and returned to a high level in agreement with the decreased corrosion rates recorded by the real-time corrosion monitoring. The impedance in the high frequency range reached a level higher than that for the new copper electrode after 5 months exposure. This is most probably mainly due to reestablishment of the thick outer porous corrosion product layer formed during 6 years pre-exposure.

The impedance data does not only confirm the impairment of the corrosion resistance during retrieval of the copper electrodes with a quite slow recovery of the corrosion resistance with time after retrieval, which was earlier observed by the real-time corrosion monitoring and the corrosion potential measurements (Fig. 4), but also shows that both the thin cuprite film and the thick porous corrosion product layer (mainly cuprite) are involved in the impairment and the recovery of the corrosion resistance. Again, the relatively high resistance of the porous layer may be due to some interplay with the corrosion products and the bentonite. This may imply that the porous corrosion product layer slowly integrates with the surrounding bentonite stabilizing the interface.

Fig. 12 illustrates the anticipated evolution of the copper interface for the new and pre-exposed copper electrodes. The corrosion resistance of pure copper in a bentonite/saline groundwater environment is presumed to depend mainly on a thin protective cuprite film that forms readily if not rapidly, and on a thick porous corrosion product layer (mainly cuprite) that develops slowly and partly intermixes with the bentonite.

The bentonite and its swelling pressure may contribute favourably to the corrosion resistance of copper in the bentonite/saline groundwater environment by means of improving the adherence of the corrosion product layers, and maybe even decreasing the porosity of the outer cuprite layer on the copper surface.

5. Conclusions

The electrochemical impedance spectra for pure copper in a bentonite/saline groundwater environment change considerably with time of exposure. The change of the spectra is more pronounced at higher than at lower frequencies. Mathematically the equivalent circuits mostly used in the literature for corrosion of copper in saline environments fit the impedance data well. However, supporting information is needed to interpret the
different parameters. Since the post-test examination of the electrodes in the present study is yet to be done, the interpretation of the data has so far been focused on the main features of the spectra.

From the impedance spectra and available information from the examination of copper coupons exposed in the same test parcel at Aspö, it is presumed that the corrosion resistance of pure copper in a bentonite/saline groundwater environment mainly depends on a thin protective cuprite film that forms readily, and on a thick porous corrosion product layer (mainly cuprite) that develops slowly and partly intermixes with the bentonite.

The pre-exposed copper electrodes were greatly disturbed during retrieval of the test parcel and test package, which caused a major change in the recorded corrosion rates and corrosion potentials, and the impedance spectra to change considerably with time thereafter both for low and high frequencies. The main reason for the disturbance is thought to be the decrease of the bentonite swelling pressure, but the drilling and cutting operations and the temperature excursion during retrieval may also have contributed. The impedance data reveals that both the inner and the outer corrosion product layer were involved in the impairment and the recovery of the corrosion resistance.

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