REAL-TIME MONITORING OF COPPER CORROSION AT THE ÄSPÖ HARD ROCK LABORATORY

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ABSTRACT

A test parcel with three cylindrical copper electrodes in one bentonite block was emplaced at the Äspö Hard Rock Laboratory in October 1999. Real-time corrosion monitoring using these copper electrodes was initiated in May 2001. The test parcel will be retrieved for post test examination in February 2005. The copper electrodes, each of about 100 cm$^2$ surface area, are exposed at a temperature of 24°C. The corrosion monitoring is performed with polarization resistance, harmonic distortion analysis and electrochemical noise techniques.

In December 2002 the instantaneous corrosion rate of the copper electrodes is 0.5 µm/y. This value is considerably lower than the average corrosion rate of about 3 µm/y estimated from retrieved copper coupons. The recorded localization factor (defined as the electrochemical current noise divided by the product between the surface area of the specimen and the corrosion current from the harmonic distortion analysis) falls in the range 0.12 to 0.15. For pure general corrosion, the localization factor
tends to be in the region of 0.01 or less, and values close to 1 are expected for severe localized corrosion. Examination of already retrieved copper coupons has not revealed any obvious signs of pitting.

Keywords: copper, bentonite, groundwater, general corrosion, localized corrosion, real-time corrosion monitoring

INTRODUCTION

A KBS-3 Repository

In Sweden the principal strategy for high-level radioactive waste disposal is to enclose the spent nuclear fuel in tightly sealed copper canisters that are embedded in clay about 500 m down in the Swedish bed-rock (named a KBS-3 repository)\textsuperscript{1,2}. The rock provides a stable and durable environment where changes occur very slowly. The canister isolates the fuel from the groundwater. The clay prevents groundwater flow around the canister and protects against minor movements in the rock. Also, when the canister is eventually breached, the bentonite clay will retain or retard the release of radio nuclides. The rock is the last barrier in this multi-barrier system between the fuel and the biosphere.

The Copper Canister\textsuperscript{2}. The copper canister consists of a 50 mm thick copper casing with a cast iron insert to provide mechanical strength. The casing is manufactured from plate of pure oxygen-free copper with a deliberate addition of approximately 50 ppm phosphorus to improve creep properties. The dimensions and waste load of each canister have been chosen such that the temperature on the outer surface of the canister never exceeds 100ºC.

The Groundwater. Groundwater in granitic rock in Sweden is oxygen-free and reducing below a depth of 100 to 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)\textsuperscript{2,3}. The chloride concentration in the groundwater can vary within very wide limits, ranging from 5 mg/dm\textsuperscript{3} to 50 g/dm\textsuperscript{3}. Groundwater analyses from different parts of Sweden show sulfide concentrations ranging from <0.01 mg/dm\textsuperscript{3} up to 1 mg/dm\textsuperscript{3}, with 0.1 mg/dm\textsuperscript{3} as a typical value. Dissolving sulfide minerals are one source of sulfide in the groundwater, but sulfide will also be produced by a specific group of microorganisms, the sulfate-reducing bacteria, which are common in deep groundwater\textsuperscript{4}.

The Bentonite Clay. The main mineral constituent in bentonite clay is montmorillonite, which has a sheet like crystal structure. As an example, Wyoming bentonite 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\textsuperscript{5}. The remaining part consists of quartz (~15 %), feldspars (~7 %), carbonates (~1.4 %), sulfides (~0.3 %), and organic carbon (~0.4 %). The mean mineralogical composition of the montmorillonite part is given by:

\[
\begin{align*}
\text{octahedral cations} & = (\text{Al}_{3.10} \text{Fe}^{3+}_{0.4} \text{Fe}^{2+}_{0.02} \text{Mg}_{0.48}) \\
\text{tetrahedral cations} & = (\text{Si}_{7.92} \text{Al}_{0.08}) \\
\text{structural O/OH} & = \text{O}_{20} (\text{OH})_{4} \\
\text{exchangeable cations} & = \text{Na}_{0.48} \text{Ca}_{0.04} \text{Mg}_{0.02}
\end{align*}
\]

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 m\textsuperscript{2}/g material and the grain density is around 2750 kg/m\textsuperscript{3}.
The Near-Field Environment. Initially, a limited amount of air will be left in a KBS-3-type repository after emplacement, which during the water saturation phase partly will be trapped by the low permeability rim of groundwater-saturated bentonite. After water saturation the chemical environment in the immediate vicinity of the canister is determined by the composition of the bentonite pore-water. This is, in turn, determined by the interaction between the bentonite and the groundwater in the surrounding rock. The entrapped oxygen will be consumed through reactions with minerals in the rock and the bentonite and also through microbial activity. The time scale of the oxic → anoxic transition has been calculated to be in the range 10 to 300 years. After the oxygen has been consumed in the repository, after a few hundred years at the very most, corrosion will be controlled completely by the supply of dissolved sulfide to the canister.

The Äspö Hard Rock Laboratory

The construction of the Äspö HRL was completed in 1995. The activities at the HRL can be regarded as a dress rehearsal for the siting and construction of the future deep repository for spent nuclear fuel. The laboratory offers a realistic environment for different experiments and tests under the conditions that will prevail in a deep repository (Figure 1). Table 1 gives a typical groundwater composition from the Äspö HRL.

The LOT Test Series. The test series “Long Term Test of Buffer Material” (LOT) has been initiated at the Äspö HRL with conditions similar to those in a final KBS-3 repository. The main purpose is to study the mineralogical stability and behavior of the bentonite clay. Wyoming bentonite with the commercial name MX-80 has been used. However, additional testing has been included, of which the investigation of corrosion on copper coupons in bentonite blocks is one.

The LOT test series comprises seven test parcels, which will be run for 1, 5 and 20 years. Each test parcel contains prefabricated bentonite blocks placed on top of each other around a central copper tube and has copper coupons in bentonite blocks 22 and 30 (Figure 2). The test parcels were placed in 4 m deep bore holes in granitic rock at a depth of 450 m below ground. The final density of the bentonite clay, at full saturation and after swelling in the test holes, was calculated to be 2000 kg/m³. Three test parcels have so far been retrieved.

Real-Time Corrosion Monitoring. As a pilot effort, cylindrical copper electrodes have been installed in one of the above test parcels, that is test parcel A2 (Figure 2), and real-time corrosion monitoring was initiated in May 2001 using a SmartCET® system. Figure 3 shows the top of the test parcel with part of the instrumentation. The system operates in a multi-technique mode, continuously cycling through the measurements in order as follows: electrochemical noise 300 s, polarization resistance and harmonic distortion analysis 100 s, and solution resistance 30 s. Electrochemical noise is the generic term used to describe the low amplitude, low frequency random fluctuations of current and potential observed in many electrochemical systems, and has been used to characterize both corrosion rate and mechanism.

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1 From InterCorr International, Houston, TX
EXPERIMENTAL PROCEDURE

Exposure of Coupons

Test coupons of pure copper are exposed in the above bentonite blocks with the objective to determine the nature and extent of corrosion. The coupons were manufactured from actual canister material (equivalent to UNS C10100 copper with a deliberate content of about 50 ppm P; 99.99 % Cu). Slots were drilled and sawed from the upper side of the bentonite blocks and the coupons were placed in the blocks during the pile up of the bentonite column. Coupons from the retrieved test parcels S1 and A0 have so far been examined.

Test Parcel S1. The copper coupons for the pilot test parcel S1 were cut by traveling-wire electric discharge machining from a plate. The nominal dimensions of the coupons are 50 x 23 x 1 mm. Test parcel S1 was emplaced on October 10, 1996. Power to the heater was first turned on October 30. Full temperature lasted from November 20, 1996, up to December 10, 1997. The overlapping core drilling around the test parcel began on January 26, 1998, and the lift-up took place on February 9. The total time of exposure is 487 days of which 385 days at full temperature. The bentonite block S122 (test parcel S1; bentonite block 22) has been exposed at a temperature of about 50°C.

Test Parcel A0. The copper coupons for test parcel A0 were machined from a plate. The coupons have milled surfaces but for one polished side. The nominal dimensions of the coupons are 60 x 15 x 1.5 mm. Test parcel A0 was emplaced on December 16, 1999. Power to the heater was first turned on February 2, 2000. Full temperature lasted from June 16, 2000, up to October 18, 2001. The test parcel was retrieved on November 27, 2001. The total time of exposure is 710 days of which 498 days at full temperature. The bentonite blocks A022 and A030 have been exposed at temperatures of about 80°C and 35°C respectively.

Test parcel A0 was situated next to test parcel A2 in which the real-time corrosion monitoring takes place.

Real-Time Corrosion Monitoring

Test parcel A2 (Figure 2), in which the real-time corrosion monitoring takes place, was emplaced on October 29, 1999. It will be retrieved in February 2005. The three cylindrical copper electrodes, each of 98.7 cm² surface area and manufactured from actual canister material, are installed in bentonite block 36 of the test parcel (Figure 2 and 4), where the temperature is about 24°C. Copper coupons are exposed in bentonite blocks A222 and A230. A groundwater composition relevant for test parcel A2 is shown in Table 18.

The real-time corrosion monitoring is performed with polarization resistance, harmonic distortion analysis and electrochemical noise techniques. Electrochemical noise data is taken at a frequency of one reading per second.

General Corrosion. The polarization resistance and the harmonic distortion analysis techniques are used to derive information regarding the general corrosion rate. A 0.01 Hz sine wave of ±25 mV is applied and the current response is measured and analyzed synchronously with the perturbing sine wave to determine the in-phase, real component of the sine wave. A value on the Stern-Geary coefficient (sometimes called the B-value) is required to calculate the corrosion rate from the measured polarization resistance data using the Stern-Geary relationship. The harmonic distortion analysis involves the meas-
urement 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.

It was earlier verified that the presently used voltage perturbation frequency of 0.01 Hz for the polarization resistance measurements is too high for measurement of the very low corrosion rates of interest\textsuperscript{15}. The polarization resistance is underestimated by a factor of 4, and thus the actual corrosion rate is overestimated to the same extent. A lower frequency could be used, but for the time being it has been decided to stay with the present set-up and instead correct the recorded values afterwards.

A default value of 10.3 mV has so far been used for the Stern-Geary coefficient based on earlier findings from a similar material – environment system\textsuperscript{16}, and a default value of n=2 in the conversion of the corrosion current to corrosion rate in µm/y using Faraday’s law.

Localized Corrosion. The electrochemical noise technique is used to derive information regarding localized corrosion. The localization factor is defined as the electrochemical current noise divided by the corrosion current from the harmonic distortion analysis (taking into account the specimen surface area; localization factor = current noise/surface area x corrosion current). As such, with purely uniform corrosion, the localization factor tends to be in the region of 0.01 or less, and values close to 1 is expected for localized corrosion.\textsuperscript{12} A value of 0.10 is interpreted as revealing only a slight tendency to local attack.

RESULTS

Average Corrosion Rates and Microscopic Observations from Exposure of Coupons

The average corrosion rates for the retrieved test coupons are summarized in Table 2. Comments about the nature of the corrosion attack are given below.

Test Parcel S1. The amount of corrosion for the first year of exposure is equivalent to an average corrosion rate of about 3 µm/y. Optical and scanning electron microscopy did not reveal any signs of pitting.

Test Parcel A0. The examined copper coupons showed about the same weight loss, in spite of the fact that coupon A022A has been exposed at about 80°C and coupon A030C at about 35°C, and the average corrosion rate was also estimated to about 3 µm/y\textsuperscript{17}. The corrosion attack is on the micro scale somewhat uneven and different corrosion products are formed along the surfaces of the coupons, however, any obvious signs of pitting cannot be claimed.

Instantaneous Corrosion Rate from Real-Time Corrosion Monitoring

Recorded Corrosion Rate. Using a measuring frequency of 0.01 Hz, a default value of 10.3 mV for the Stern-Geary coefficient, and n=2 for the number of electrons in Faraday’s law, the recorded corrosion rate has varied from 2.8 to 2.1 µm/y up to December 2002, ignoring the very first period after start of the measurements in May 2001 (Figure 5).

Recorded Stern-Geary Coefficient. The recorded value of the Stern-Geary coefficient in December 2002 is 6.5 mV and has varied between 6.5 and 6.7 mV (Figure 6).
Best Estimate of the Corrosion Rate. With corrections for the used voltage perturbation frequency and the Stern-Geary coefficient, the actual corrosion rate is estimated to be less than 0.7 μm/y for \( n=1 \) and less than 0.35 μm/y for \( n=2 \). Considering the surface appearance of the retrieved copper coupons revealing both Cu(I) and Cu(II) corrosion products, half ways in between these two values, that is 0.5 μm/y, might well be the best estimate of the corrosion rate of copper in bentonite block A236 in December 2002. However, this is too early to claim; further verification is needed.

Tendency to Localized Corrosion

The recorded localization factor has increased slightly from 0.12 to 0.15 in December 2002 ignoring the very first period after start of the measurements in May 2001 (Figure 7). These values are interpreted as indicating only a slight tendency to local attack. (This can unfortunately not be verified until the test parcel will be retrieved in February 2005.)

DISCUSSION

General Corrosion

Can the polarization resistance method be applied? The amount of oxidants in the bentonite block with the electrodes is limited, which means mass-transfer control. However, the polarization resistance method should also be applicable for this case.

What are the requirements? In order to obtain the true corrosion rate for copper in repository environments from polarization resistance measurements, it is at least necessary to (i) be able to measure low corrosion rates, (ii) fulfill requirements for steady-state conditions, (iii) consider possible interfering redox systems, (iv) pay attention to the measuring frequency used by the electronic equipment, (v) consider the solution resistance, (vi) measure and use the proper Stern-Geary coefficient in the calculations, and (vii) use the proper \( n \)-value in the calculations using Faraday’s law. Here follows a few comments to these items:

(i) The used corrosion monitoring system is capable of measuring sufficiently low corrosion activity.
(ii) It is believed that steady-state conditions are fulfilled soon after the groundwater has penetrated the bentonite. The emplacement of the test parcel took place on October 29, 1999, and the real-time corrosion monitoring commenced in May 2001.
(iii) It is assumed that there is no interfering redox system of sufficient magnitude, but this may not yet have been considered in depth.
(iv) The underestimation of the polarization resistance at a measuring frequency of 0.01 Hz, and thus the overestimation of the corrosion rate, has indirectly been checked (so far without the presence of bentonite) by means of electrochemical impedance measurements using a laboratory set-up with the canister material exposed to synthetic bentonite-equilibrated groundwater\(^{15}\).
(v) The equipment measures the solution resistance.
(vi) The equipment measures the actual Stern-Geary coefficient.
(vii) The software uses a default value of \( n=2 \), which could be questioned; to assure a conservative estimate it might have been better to use \( n=1 \). (In the best estimate calculation above, half \( n=1 \) and half \( n=2 \) has been used.)
How conservative is the corrosion rate estimate? If we assume that steady-state conditions are established, that the corrosion monitoring system picks up all electrochemical activity, that the solution resistance is so low that it can be ignored, and disregards any interfering redox systems, then the recorded corrosion rate is quite conservative. The degree of overestimation of the corrosion rate depends on the applied measuring frequency and the value of the Stern-Geary coefficient in the calculation. Without any corrections we end up with a corrosion rate of 2.1 µm/y, if we make the proper corrections the corrosion rate estimate falls in the range 0.35 µm/y for (n=2) to 0.7 µm/y (for n=1).

Localized corrosion

How trustworthy is electrochemical noise to give information about localized corrosion? Electrochemical noise is a quite new technique, that is very attractive for real-time corrosion monitoring. However, it is important to correlate the findings with other observations, such as from exposure of coupons or from other electrochemical testing.

What is the meaning of the recorded localization factor? It is too early to try to elucidate the meaning of the recorded localization factor. However, a value of the order of 0.1 is believed to indicate a tendency to localized attack, but an inability to maintain the attack. Post test examination of the copper electrodes, and the copper coupons, after retrieval of the test parcel in February 2005 will hopefully give a great deal of information about the matter.

Back-up Laboratory

In order to further penetrate the above questions and support the field measurements at the Äspö HRL, laboratory work has been initiated at the Royal Institute of Technology in Stockholm using the very same corrosion monitoring equipment combined with other equipment and techniques.

CONCLUSIONS

As a pilot effort real-time monitoring of copper corrosion has been applied at the Äspö HRL since May 2001. The experience gained so far support the idea that it is possible to measure very low instantaneous corrosion rates of copper in bentonite saturated with groundwater. With corrections for the measuring frequency and the actual Stern-Geary coefficient, and using both n=1 and n=2 in the Faraday’s law conversion to equal extent, a reasonable guess of the best estimate of the corrosion rate of copper three years after emplacement of the test parcel is considered to be 0.5 µm/y. It can be argued how well founded this estimate is, and additional work will be pursued to find out.

The real-time corrosion monitoring indicates, by showing a localization factor of about 0.14, a tendency to localized attack. The copper coupons from the retrieved test parcels have a somewhat uneven corrosion attack with different corrosion products on the surfaces, but no obvious signs of pitting.

Additional work will be pursued to further qualify the readings from the real-time monitoring of copper corrosion at the Äspö HRL.
ACKNOWLEDGMENTS

The contributions from the staff at the Äspö HRL, and from Graham Quirk and Jason Duncan of InterCorr International during start of the measurements, are gratefully acknowledged.

REFERENCES

10. SmartCET® Technology – User Guide v06 04 03, InterCorr International, Houston, TX.
17. B. Rosborg, unpublished results.
### TABLE 1
A TYPICAL GROUNDWATER COMPOSITION FROM THE ÅSPÖ HRL

<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>6410</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>181</td>
<td>560</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.2</td>
<td>0.15</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>HS⁻</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>$E_{\text{redox}}$ mV SHE</td>
<td>-308</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 2
AVERAGE CORROSION RATE FOR COPPER COUPONS IN RETRIEVED BENTONITE BLOCKS

<table>
<thead>
<tr>
<th>Specimen No</th>
<th>Specimen Size (mm)</th>
<th>Temperature (°C)</th>
<th>Time Period of Exposure</th>
<th>Days of Exposure</th>
<th>Days at Full Temperature</th>
<th>Average Corrosion Rate (µm/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S122A</td>
<td>50x23x1</td>
<td>50</td>
<td>Nov 1996 - Feb 1998</td>
<td>487</td>
<td>385</td>
<td>2.7-3.4</td>
</tr>
<tr>
<td>A022A</td>
<td>60x15x1.5</td>
<td>80</td>
<td>Dec 1999 - Nov 2001</td>
<td>710</td>
<td>498</td>
<td>2.4-3.5</td>
</tr>
<tr>
<td>A030C</td>
<td>60x15x1.5</td>
<td>35</td>
<td>Dec 1999 - Nov 2001</td>
<td>710</td>
<td>498</td>
<td>2.4-3.4</td>
</tr>
</tbody>
</table>

1. First figure based on total number of days and second figure based on number of days at full temperature.

### TABLE 3
REAL-TIME MONITORING DATA OF COPPER CORROSION IN BENTONITE BLOCK A236

<table>
<thead>
<tr>
<th>Time</th>
<th>Recorded Corrosion Rate (µm/y)</th>
<th>Recorded Stern-Geary coefficient (mV)</th>
<th>Recorded Localization Factor</th>
<th>Best Estimate of the Corrosion Rate (µm/y)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jul-01</td>
<td>2.8</td>
<td>6.6</td>
<td>0.12</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>Dec-01</td>
<td>2.3</td>
<td>6.6</td>
<td>0.14</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Jun-02</td>
<td>2.3</td>
<td>6.6</td>
<td>0.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dec-02</td>
<td>2.1</td>
<td>6.5</td>
<td>0.15</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

1. Measuring frequency 0.01 Hz, default value of 10.3 mV for the Stern-Geary coefficient, and $n=2$ in Faraday’s law.
2. Correction for the too high measuring frequency by a factor of ¼, the actual value for the Stern-Geary coefficient, and using both $n=1$ and $n=2$ to equal extent, that is $n=1.5$, in Faraday’s law.
FIGURE 1 – Äspö Hard Rock Laboratory

FIGURE 2 – Test parcel A2

FIGURE 3 – Top of test parcel A2

FIGURE 4 – Bentonite block A236

Sensors:
- Electro chemical noise sensor
- Copper rod 
  \( \phi = 29.7 \text{mm} \)
  \( L = 90.0 \text{mm} \)
FIGURE 5 – The recorded corrosion rate of copper in bentonite block A236

FIGURE 6 – The recorded Stern-Geary coefficient for copper in bentonite block A236

FIGURE 7 – The recorded localization factor for copper in bentonite block A236