

Real-time monitoring of copper corrosion at the Äspö HRL

Bo Rosborg^a, David Eden^b, Ola Karnland^c, Jinshan Pan^a, and Lars Werme^d

^aRoyal Institute of Technology, Div. Corrosion Science, Drottning Kristinas väg 51, SE – 100 44 Stockholm, Sweden

bo.rosborg@telia.com and jinshanp@kth.se

^bInterCorr International, Inc., 14503 Bammel-N Houston, Suite 300, Houston, TX 77014, USA, *daeden@intercorr.com*

^cClay Technology AB, Ideon Research Center, SE – 223 70 Lund, Sweden
ok@claytech.se

^dSvensk Kärnbränslehantering AB, P.O. Box 5864, SE – 102 40 Stockholm, Sweden
lars.werme@skb.se

Abstract

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 bentonite clay about 500 m down in the Swedish bed-rock. Initially, a limited amount of air will be left in a repository after emplacement. The entrapped oxygen will be consumed through reactions with minerals in the rock and the bentonite and also through microbial activity. 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 sulphide to the canister. The present work concerns the oxic period after emplacement. The main hypothesis is that the average corrosion rate of the canister under oxic conditions will be less than 7 $\mu\text{m}/\text{year}$, and that pitting will only be possible under these conditions.

The Äspö Hard Rock Laboratory offers a realistic environment for different experiments and tests under the conditions that will prevail in a deep repository. Real-time monitoring of copper corrosion is presently performed with polarization resistance, harmonic distortion analysis and electrochemical noise techniques. The first two techniques are used to derive information regarding the general corrosion rate and the third to derive information regarding localized corrosion. In order to support these measurements at Äspö, laboratory work is also performed at the Royal Institute of Technology in Stockholm using the very same corrosion monitoring equipment and also other equipment and techniques. Copper coupons are also exposed at Äspö.

Results from the work at Äspö and in Stockholm are presented with an emphasis on the gained information concerning localized corrosion. The recorded corrosion rates at Äspö are well below the value given above, and the recorded localization factors are interpreted as indicating only a slight tendency to local attack.

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

Background

Requirements and conditions [1]

According to Swedish law, anyone who generates electricity by means of nuclear power must also manage and dispose of the waste in a safe manner. In 1976 the Swedish government required that the reactors that are under construction may only be started if certain stipulations are fulfilled. As a response the utilities launched the so-called KBS project (where KBS stands for “KärnbränsleSäkerhet”, that is Nuclear Fuel Safety). Early work also considered reprocessing, but in “the third report”, published in 1983, a method for direct disposal was presented [2]. The report recommends a final repository in the Swedish crystalline bedrock with barriers of natural materials. It is today called the KBS-3 method.

The deep repository for spent nuclear fuel must be safe and isolate the fuel for 100 000 years. After around 100 000 years the radioactivity of the fuel is down to the same level as in the enriched uranium from which the fuel was made.

The Swedish nuclear power utilities have jointly formed Svensk Kärnbränslehantering AB (SKB, the Swedish Nuclear Fuel and Waste Management Company). The company is responsible for research, development, planning, construction, and operation of the waste facilities. Regulatory authorities and the Government oversee its work.

SKB has chosen to build the repository with materials that occur naturally in the earth’s crust and according to the multiple barrier principle. According to the plan, canister deposition will begin in about 15 years. To start with part of the needed canisters will be deposited and the remaining canisters will be deposited following an evaluation.

A KBS-3 repository [3]

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, see Figure 1. 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 radionuclides. The rock is the last barrier in this multi-barrier system between the fuel and the biosphere.

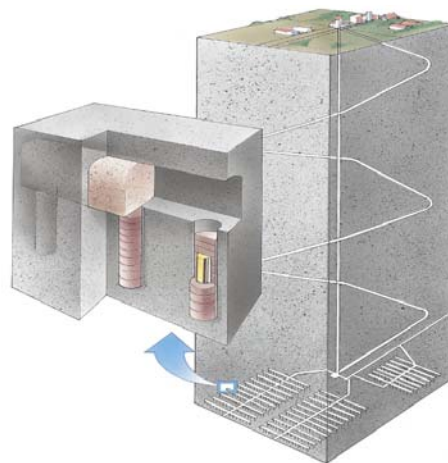


Fig. 1 A KBS-3 repository.

Why copper? [4]

Copper is very corrosion resistant in natural environments: “Copper alloy artefacts have been found in nearly pristine condition after having been buried in the earth for thousands of years, ...” [5]. Native copper has been preserved for nearly 200 million years in an environment, which is similar to the repository near-field environment [6-7]. However, we also know that copper shows inadequate corrosion resistance in some environments.

The long-term corrosion behaviour of copper as canister material was first assessed in 1978 by the Swedish Corrosion Institute [8], and a re-assessment of the predicted canister lifetime in a KBS-3-type repository was recently performed [9-11].

It has been shown that general corrosion will not pose a threat to the canister integrity. Even with very pessimistic assumptions, the maximum corrosion attack during 100 000 years should not exceed 5 mm, and will probably not exceed a few tenths of a millimeter [4,9]. The main hypothesis is that the average corrosion rate of the canister under oxic conditions, see below, will be less than 7 $\mu\text{m}/\text{year}$ [12]. Under anoxic conditions, the sulphide in the groundwater will corrode the copper. The low sulphide content of the groundwater in combination with the very low water exchange rate at the canister surface will lead to a corrosion rate determined by the mass transfer of sulphide to the copper canister surface. The rate will depend on sulphide content in the groundwater and in the bentonite buffer and will be in the range of 10-2 $\mu\text{m}/\text{year}$ or lower. This situation could be dramatically changed if the sulphate reducing bacteria were to form a biofilm on top of the copper surface. Experimental studies have shown, however, that this is an extremely unlikely situation since the sulphate reducing bacteria cannot survive in the compacted bentonite surrounding the canister [13].

The likelihood for pitting of the copper canister in a repository environment is low, and may not even exist. However, the possibility for pitting cannot be completely ruled out. Pitting will only be possible under oxic conditions [9]. A pitting factor of 5 or less has been used as a realistic estimate in assessing the lifetime of the canister in the repository [12].

The selected material-environment system should ensure satisfactory corrosion behaviour.

The material-environment system

The copper canister [4]

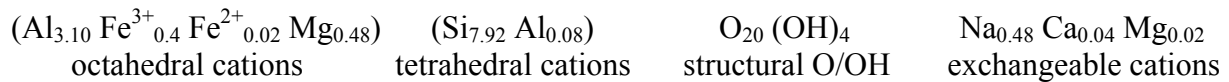
The copper canister in its present design consists of a 50 mm thick copper casing with a cast iron insert to provide mechanical strength. The casing is manufactured from plate of pure oxygen-free copper with a deliberate addition of approximately 50 ppm phosphorus to improve creep properties. The dimensions and waste load of each canister have been chosen such that the temperature on the outer surface of the canister never exceeds 100°C.

The groundwater [8,14]

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) [4,15]. The chloride concentration in the groundwater can vary within very wide limits, ranging from 5 mg/dm^3 to 50 g/dm^3 . Groundwater analyses from different parts of Sweden show sulphide concentrations ranging from $<0.01 \text{ mg}/\text{dm}^3$ up to 1 mg/dm^3 , with 0.1 mg/dm^3 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 microorganisms, the sulphate-reducing bacteria, which are common in deep groundwater [16].

The bentonite clay [17]

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. 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:



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 near-field environment [9,18]

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 porewater. 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 [18]. 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 sulphide to the canister.

“The challenge”

Besides rock movements the biggest threat to the canister in the repository is corrosion.

How to prove/how to verify? – Means and methods [9]

Different means and methods have been used to gain a well-founded basis to predict the corrosion behaviour of the copper canister and the engineering barrier integrity, including thermodynamic considerations, field and laboratory testing, modelling of the corrosion behaviour, and examination of natural and archaeological analogues. A comprehensive review of the existing knowledge of copper corrosion of relevance for the repository environments was performed in 2001 [9-11].

The time at disposal to further expand the database to predict container integrity is not more than 15 years. Exposure of copper coupons during 15 years at the most is still strikingly short considering required canister life. Thus, also other ways of gaining additional information is of interest.

A further possibility?

Real-time monitoring of copper corrosion in actual or simulated repository environments offers a further possibility to improve the basis to predict the corrosion behaviour of the copper canister.

Different real-time monitoring techniques are available. Among these the electrochemical techniques offer the best sensitivity, and some of them also have the desirable possibility to provide information about the degree of localization of the corrosion attack. While exposure of coupons give information about the average corrosion behaviour from start of exposure, the electrochemical methods give more or less instantaneous information. When adopting electrochemical methods faster and more detailed information is acquired.

However, to assure correct interpretation of recorded electrochemical data, the methods have to be correlated to actual corrosion behaviour. Thus, the question is not either electrochemical methods or exposure tests; a both-and approach is needed.

Today robust instrumentation for field applications is available.

In order to find out the possibilities and limitations with real-time monitoring of copper corrosion in repository environments by means of electrochemical methods, a pilot effort is in progress at the Äspö Hard Rock Laboratory since a few years [19].

The Äspö Hard Rock Laboratory

The Äspö HRL consists of a 3 600 m long spiral tunnel that goes down to a depth of 460 m (Figure 2). The construction of the underground laboratory 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.

Table 1 gives a typical groundwater composition from the Äspö HRL [15].

The pilot effort with real-time monitoring of copper corrosion is performed on electrodes placed in LOT test parcel A2, see below [20]. Recently measurements have also been performed on electrodes placed in the Prototype Repository deposition holes 1 and 5. The two experiments are performed in tunnels next to each other in the Äspö HRL, see Figure 2.

The LOT test series [17,20-21]

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 behaviour 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 rings 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 rings placed on top of each other around a central copper tube and has copper coupons in bentonite rings 22 and 30 (Figure 3). 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.

Test parcel A2 with the copper electrodes for the real-time monitoring was emplaced on October 29, 1999. The three cylindrical copper electrodes, each of 98.7 cm² surface area, have been installed in bentonite ring 36 of the test parcel. Thus, the electrodes are positioned near the top of the test parcel, see Figure 3, where the temperature is about 24°C. Figure 4 shows

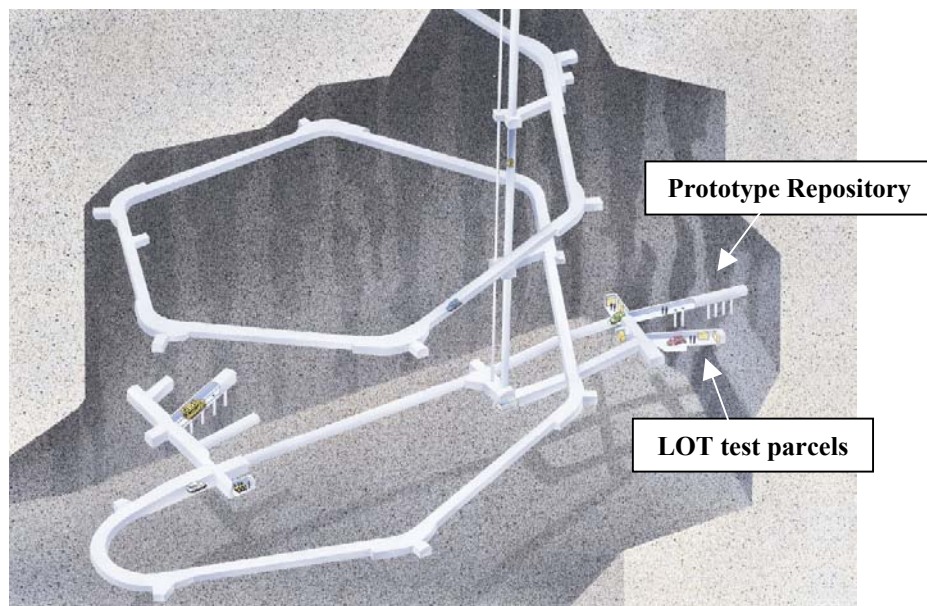


Fig. 2 Äspö Hard Rock Laboratory.

Table 1. A typical groundwater composition from the Äspö HRL.

Ion	mM	mg/dm ³
Na ⁺	91	2 100
K ⁺	0.2	8
Ca ²⁺	47	1 890
Mg ²⁺	1.8	42
Cl ⁻	181	6 410
HCO ₃ ⁻	0.2	10
SO ₄ ²⁻	5.8	560
HS ⁻	0.005	0.15
pH 7.7	E _{redox} -308 mV SHE	

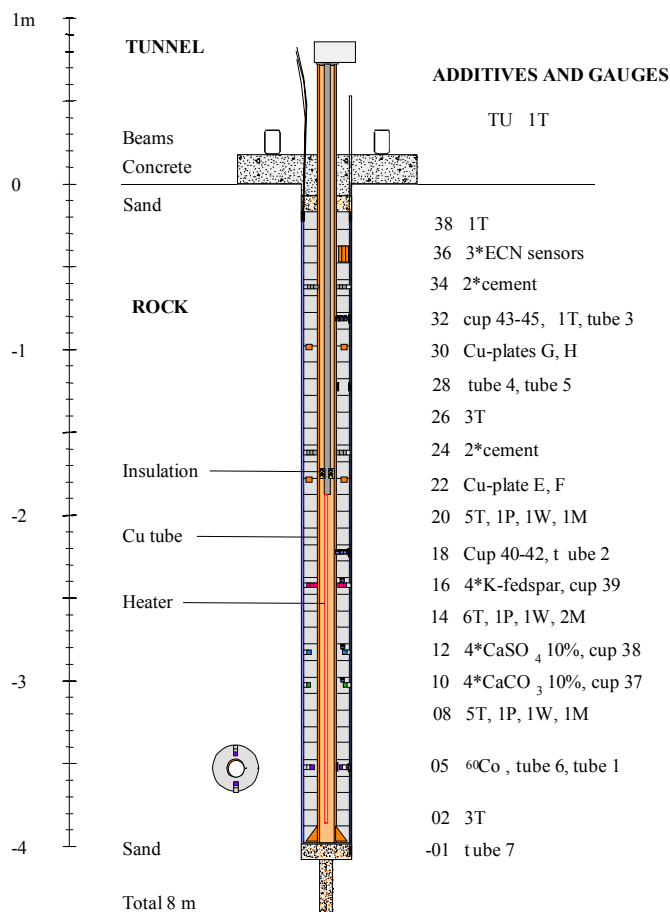


Fig. 3 LOT test parcel A2.

the top of the test parcel with part of the instrumentation. The electrode arrangement in bentonite ring A236 is shown in Figure 5.

The Prototype Repository [21]

The “Prototype Repository” consists of a bored deposition tunnel with six full-scale canisters deposited in the same manner as in the future deep repository. It is divided in an inner and an outer section. Electrical heaters generate the heat output from the canisters. The deposition holes are 8 m deep and just under 2 m in diameter. Each deposition hole is lined with blocks and rings of bentonite. All components in the Prototype Repository have the same dimensions as they will have in the real deep repository.

Cylindrical copper electrodes were also installed in Prototype Repository deposition holes 1 and 5 to make real-time corrosion monitoring possible. The electrodes have a surface area of about 232 cm² each, and were installed in the second upper bentonite block in deposition hole 1 and in the upper block in deposition hole 5. Thus, the electrodes are positioned above the canisters.

The inner section of the Prototype Repository with four canisters was sealed during 2001 and the outer during 2003. For deposition hole 1 in the inner section heat has been on since September 17, 2001, and for deposition hole 5 in the outer section heat has been on since May 8, 2003.



Fig. 4 Top of LOT test parcel A2 with part of the monitoring equipment.

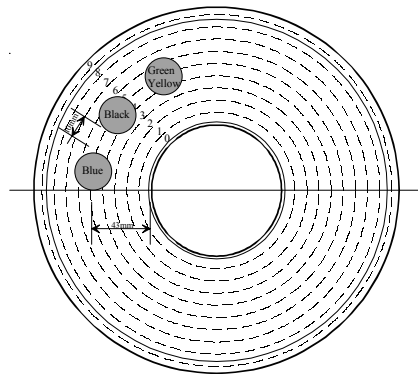


Fig. 5 Electrode arrangement in bentonite ring A236.

Real-time corrosion monitoring at Äspö

The real-time corrosion monitoring at Äspö is performed with a SmartCET^{®(1)} corrosion monitoring system. The measurements were initiated on the electrodes in LOT test parcel A2 in May 2001 [19], and the first measurements on the electrodes in Prototype Repository deposition holes 1 and 5 were performed in January 2004. For the results presented below the very same SmartCET[®] system has been used.

Monitoring equipment and techniques

The SmartCET[®] corrosion monitoring 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) [22].

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

¹ From InterCorr International, Inc., Houston, TX

has been used to characterize both corrosion rate and mechanism [23-24]. Electrochemical noise data is taken at a frequency of one reading per second.

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 analysed 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 recorded polarization resistance data using the Stern-Geary relationship [25]. 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 [26], and a default value of $n=2$ is used for conversion of the corrosion current to corrosion rate using Faraday's law. The polarization resistance technique is useful for measurement of the corrosion rate when corrosion is relatively uniform, but it has some limitations [27]. It is assumed that the system under study has reached steady state when the measurement is made, and the measured polarization resistance is a composite of the solution resistance and the charge-transfer resistance.

Harmonic distortion analysis relies on the non-linear nature of electrochemistry and is related to electrochemical impedance spectroscopy, in that an alternating potential perturbation is applied to one sensor element in a three-element probe, measuring a resultant current response [28]. Here 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.

It was earlier verified that the presently used voltage perturbation frequency of 0.01 Hz is too high for measurement of the very low corrosion rates of interest [29]. The polarization resistance is underestimated by a factor of about 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.

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, and is used for evaluation of the tendency to local attack. 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 [24]. A value of 0.10 is interpreted as revealing only a slight tendency to local attack.

Electrochemical noise measurement is a quite new technique. It is very attractive for real-time corrosion monitoring, since it has the potential of providing information about the localization of the corrosion attack. However, it is important to correlate the noise data with actual corrosion behaviour.

Sequence of measurements

Normally one of the electrodes in a three-electrode set-up is picked as the working electrode, one as the pseudo reference electrode, and the third as the counter electrode (the second working electrode for electrochemical noise measurements). However, if the electrodes are identical (at least at the time of installation) there are six possibilities to connect the electrodes to the monitoring equipment: the three electrodes can in turn be the working electrode, and the remaining two electrodes could either function as the pseudo reference or the counter

electrode. This possibility has been used for the measurements presented below for both the electrodes in LOT test parcel A2 and in Prototype Repository deposition holes 1 and 5. The reason for such a procedure is to obtain additional information about spread in data and possible asymmetry of the corrosion attack on the three electrodes.

For each electrode combination at least five recordings have been taken with the monitoring system before changing to the next electrode combination, which means that the measurement duration for each combination has been about 30 min (ignoring the time in between changes).

Back-up laboratory work at KTH

The field measurements at Äspö are supported by laboratory work at the Royal Institute of Technology (KTH) in Stockholm using the very same corrosion monitoring equipment, and also other equipment and techniques. So far these laboratory experiments have, however, only been carried out in stagnant synthetic groundwater open to air without the presence of bentonite. One laboratory set-up with cylindrical copper electrodes is shown in Figure 6.

Note: Granitic groundwater has Ca^{2+} concentrations of several hundred to a few thousand ppm at a depth of 500 m (5 MPa pressure). In the laboratory experiments, the calcium content has been replaced with sodium to avoid the precipitation of calcite that would occur at atmospheric pressure. The assumption is that this modification will not alter the corrosion behaviour of copper.

The work at KTH includes electrode impedance measurements to gain information for proper correction of recorded corrosion rates [29], a study of the influence of deliberate surface defects on the corrosion resistance of pure copper [30], and experiments for interpretation of the meaning of recorded localization factors.



Fig. 6 Example of present laboratory set-up.

Results and experiences

Instrumental

The corrosion monitoring equipment has proved to be capable of measuring very low corrosion rates of copper in repository environments with an apparent resolution of $< 0.1 \mu\text{m}/\text{year}$. The presently used measuring frequency of 0.01 Hz is, however, not low enough for this application and the recorded corrosion rates are quite conservative [29]. Work to modify the equipment to also handle lower measuring frequencies is in progress. However, to apply a

lower measuring frequency means longer measuring periods and demands on the stability of the electrodes. The presently used measuring frequency, combined with corrections of the recorded corrosion rates afterwards, may well be a suitable choice.

For field measurements, such as those performed on the electrodes in Prototype Repository deposition holes 1 and 5, very long cables are needed. This has turned out to be no problem [31].

Corrosion behaviour

Recorded data from measurements on all electrodes in the three-electrode set-ups at Äspö with the very same equipment is exemplified in Tables 2 through 4. For further information about recorded corrosion rates, see Refs. 27 and 29. A summary of the measured localization factors is given in Table 5.

Note: The corrosion rate data given in the tables below is not corrected for the measuring frequency; thus, the actual corrosion rates are considerably lower [29].

Table 2. Corrosion rates¹ and localization factors recorded on 2004-02-11 for the copper electrodes in LOT test parcel A2.

Working electrode	Corr rate ² µm/year	Corr rate ³ µm/year	Localization factor	Stern-Geary coefficient, mV
Black	1.85	1.80	0.13	7.0
	1.67	1.63	0.14	6.8
Blue	1.50	1.47	0.11	7.0
	1.36	1.32	0.13	6.9
Yellow-green	2.32	2.27	0.11	7.0
	2.53	2.47	0.10	7.1
<i>All, range</i>	<i>1.36-2.53</i>	<i>1.32-2.47</i>	<i>0.10-0.14</i>	<i>6.8-7.1</i>
<i>All, median</i>	<i>1.85</i>	<i>1.80</i>	<i>0.13</i>	<i>7.0</i>

Notes to Tables 2 through 4:

1. Not corrected for the used measuring frequency [29].
2. Corrosion rate based on polarization resistance measurements and corrected for the actual Stern-Geary coefficient.
3. Corrosion rate based on harmonic distortion analysis.

Table 3. Corrosion rates¹ and localization factors recorded on 2004-02-12 for the copper electrodes in Prototype Repository deposition hole 1.

Working electrode	Corr rate ² µm/year	Corr rate ³ µm/year	Localization factor	Stern-Geary coefficient, mV
Black	0.51	0.50	0.07	7.2
	0.54	0.53	0.07	7.2
Blue	0.52	0.51	0.07	7.2
	0.50	0.49	0.07	7.3
Yellow-green	0.44	0.43	0.07	7.6
	0.47	0.46	0.07	7.4
<i>All, range</i>	<i>0.44-0.54</i>	<i>0.43-0.53</i>	<i>0.07</i>	<i>7.2-7.6</i>
<i>All, median</i>	<i>0.51</i>	<i>0.50</i>	<i>0.07</i>	<i>7.3</i>

Table 4. Corrosion rates¹ and localization factors recorded on 2004-02-12 for the copper electrodes in Prototype Repository deposition hole 5.

Working electrode	Corr rate ² µm/year	Corr rate ³ µm/year	Localization factor	Stern-Geary coefficient, mV
Black	0.18	0.18	0.04	10.6
	0.16	0.16	0.03	10.7
Blue	0.06	0.06	0.04	11.0
	0.06	0.05	0.10	10.4
Yellow-green	0.24	0.23	0.02	11.6
	0.17	0.16	0.03	10.9
<i>All, range</i>	<i>0.06-0.24</i>	<i>0.05-0.23</i>	<i>0.02-0.10</i>	<i>10.4-11.6</i>
<i>All, median</i>	<i>0.17</i>	<i>0.16</i>	<i>0.04</i>	<i>10.9</i>

Table 5. Recorded localization factors for corrosion of copper in bentonite blocks and rings at the Äspö HRL.

Experiment	Time	Localization factor	
		Median	Range
LOT test parcel A2	Dec '01	0.14	
	Dec '02	0.15	
	Dec '03	0.10	
	Jan '04	0.10	
	Feb '04	0.12	0.10 – 0.14
	May '04	0.11	0.09 – 0.13
Prototype Repository Deposition hole 1	Jan '04	0.07	0.07
	Feb '04	0.07	0.07
	Mar '04	0.07	0.07 – 0.08
Prototype Repository Deposition hole 5	Jan '04	0.03	0.02 – 0.04
	Feb '04	0.04	0.02 – 0.10
	Mar '04	0.02	0.02 – 0.04

Note: Data for LOT test parcel A2 up to February '04 are from one electrode combination only. The remaining data are from all electrode combinations (see “Sequence of measurements” above), which is obvious from Tables 2 through 4.

As a comparison Table 6 shows data from measurements at KTH with cylindrical copper electrodes in stagnant synthetic “bentonite equilibrated” groundwater open to air at room temperature. The compositions of the two solutions are given as notes to Table 7. Experimental details are found in Ref. 30. The corrosion rates are as expected considerably higher compared to the Äspö data. However, the localization factors are quite similar.

Compilation and interpretation of data

Recorded localization factors at Äspö and at KTH

The recorded localization factors for pure copper in bentonite blocks and rings at Äspö and in stagnant synthetic “bentonite equilibrated” groundwater open to air at KTH are summarized in Table 7. All data fall below 0.15.

Table 6. Corrosion rates and localization factors for copper electrodes in stagnant synthetic bentonite equilibrated groundwater open to air at room temperature (no bentonite present)¹.

Experiment	Duration	Corr rate ² µm/year	Localization factor	Stern-Geary coefficient, mV
1 smooth ³ defected ⁴	02-05-27 – 02-06-18		0.03 – 0.06 <0.01 – 0.07	
2 smooth defected	02-12-18		0.02 – 0.03 0.04 – 0.06	
3 smooth defected	04-05-18	9 – 11 13 – 15	0.01 – 0.07 0.03 – 0.11	11.1 – 12.5 9.5 – 10.5

Notes:

1. For information about the groundwater composition see the notes to Table 7; experiments 2 and 3 have been performed in an environment based upon a groundwater analysis from Äspö.
2. Corrosion rate based on polarization resistance measurements and corrected for the actual Stern-Geary coefficient. However, not corrected for the used measuring frequency [29].
3. Three-element probe with smooth specimens.
4. Three-element probe with either one (experiment 1) or two deliberately defected specimens in working electrode positions.

Table 7. Localization factors for corrosion of pure copper in bentonite/groundwater.

Laboratory	Experiment	Localization factor	Ref
Äspö HRL	LOT test parcel A2	0.09 – 0.15	19
	Prototype Repository	0.02 – 0.10	
KTH	Synthetic Äspö groundwater ¹	0.01 – 0.11	31
	Another groundwater ²	<0.01 – 0.07	30

Notes:

1. Bentonite equilibrated; Na⁺ to match pH=9.0, NH₄⁺ 0.5, Cl⁻ 6940, HCO₃⁻ 60, SO₄²⁻ 480 mg/dm³ respectively.
2. Bentonite equilibrated; Na⁺ 17240, NH₄⁺ 0.5, Cl⁻ 19200, HCO₃⁻ 600, SO₄²⁻ 9600 mg/dm³ respectively; pH=9.0.

Comparison to localization factors from a few other material-environment systems [32]

For carbon steel systems undergoing relatively fast uniform corrosion (>250 µm/year) a localization factor of <0.01 is typically observed. As the general corrosion rate falls, the propensity for localized corrosion increases, and micro pitting in carbon steel produces values in the range 0.01 to 0.1. This corresponds to a relatively high pit distribution. With “passivated” carbon steel, for example with nitrite inhibitor, chloride ions will initiate pitting and lead to localization factors >0.1.

For severe pitting environments, the passive materials (for example stainless steels and aluminium) show very high localization factors, often >1, due to the low general corrosion rates and high levels of electrochemical noise from the pitting activity.

Table 8 gives examples of localization factors for carbon steel, stainless steel and aluminium systems.

Table 8. Localization factors (LF) for other material-environment systems [32].

Material	Application/Environment	Form of corrosion	LF
Carbon steel	Offshore platform “slop tank”	Pitting	>0.5
	Offshore platform “slop tank”	General corrosion	<0.1
	12” Gas Receiving Line	Pitting	>0.3
	8” Gas Processing Line	General corrosion	<0.02
Stainless steel	Sea water	Pitting	>0.5
	NaCl/FeCl ₃ pH2	General corrosion	0.01-0.1
	0.1 % NaSO ₄ solution	General corrosion	0.01
Aluminium	Sea water	Pitting	>0.1

Information gained from exposed copper specimens

Observations after exposure of copper specimens in actual and simulated repository environments are shown in Table 9. The average corrosion rates for the copper coupons from the retrieved LOT test parcels fall below 3.5 $\mu\text{m}/\text{year}$ [17,27]. 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. A picture of a copper coupon after removal from the bentonite ring and ultrasonic cleaning in water is shown in Figure 7. (Corrosion products remained on the bentonite surfaces.)

Long-term laboratory tests with small copper canisters in bentonite/groundwater have not revealed pitting [33]. A rough surface attack on copper, named “under-deposit corrosion”, has been reported from a Canadian study [34]. However, the corrosion attack is considered to be an uneven general attack rather than pitting. A follow-up study has confirmed this [35].

Table 9. Observations after exposure of copper specimens in actual or simulated repository environments.

Specimen	Experiment	Exposure time	Observation	Ref
S122A	Äspö LOT test parcel S1; 50°C	385 days	No obvious signs of pitting	17,27
A022A	Äspö LOT test parcel A0; 80°C	498 days		27
A030C	Äspö LOT test parcel A0; 35°C	498 days		27
	Bentonite; groundwater, three compositions; 80°C		No indication of pitting	33
	Simulating Canadian repository environment		Under-deposit corrosion	34
	Under-deposit corrosion		No discrete pitting	35



Fig. 7 Appearance of copper coupon S122A after exposure and ultrasonic cleaning in water.

Present interpretation of the Äspö recordings

What do the recorded localization factors for corrosion of copper actually mean?

It is too early to try to elucidate an in depth interpretation of the recorded localization factors. More information is needed. However, based upon the available information from the pilot effort, the supporting laboratory measurements, the examination of retrieved copper coupons at Äspö, and some other available information, the recorded localization factors of the order of 0.1 are believed to indicate a tendency to localized attack, but an inability to maintain the attack. Post test examination of the LOT test parcel A2 copper electrodes, and the copper coupons in the test parcel, after retrieval early next year will hopefully give valuable information about the matter.

Next efforts

The present pilot effort may be considered as the first step in a step-by-step evaluation of the usefulness with real-time monitoring of copper corrosion in repository environments by electrochemical methods. The obtained experience and results show that such measurements are feasible.

It is unfortunate that the real-time corrosion monitoring in the pilot effort is performed on one set of specimens, while the gravimetric data is obtained from another set of specimens. For evaluation purposes it would have been better if the electrochemical and the weight loss data were from the very same specimens. One reason for this deficiency is lack of time between the idea of performing the pilot effort and the actual emplacement of the test parcels. Another reason is that robust cylindrical electrodes were preferred for the installation in the bentonite blocks and rings in spite of the fact that their dimensions are inappropriate for gravimetric determination of low corrosion rates. In other words, the first priority was to select reliable conditions for the real-time monitoring. In a next step a more detailed verification of the measured data can be done.

The next efforts at Äspö comprises (i) completion of the present corrosion monitoring on LOT test parcel A2, possibly supplemented by further measurements on the electrodes in Prototype Repository deposition holes 1 and 5; (ii) planning of a follow-up experiment; (iii) retrieval of LOT test parcel A2 early next year followed by a careful examination of the copper electrodes in bentonite ring A236, and the copper coupons in bentonite rings A222 and A230; and (iv) later also examination of copper coupons from the remaining LOT test parcels.

The next efforts at KTH comprises (i) completion of the work with deliberately defected specimens; (ii) qualification of the meaning and interpretation of the localization factor; and (iii) experiments in bentonite/groundwater (for a better simulation).

Summary and conclusions

A pilot effort with real-time monitoring of copper corrosion is performed at the Äspö Hard Rock Laboratory (primarily on copper electrodes in LOT test parcel A2) with back-up laboratory work at KTH in Stockholm.

The corrosion monitoring equipment has proved to be capable of measuring very low corrosion rates (with an apparent resolution of $<0.1 \mu\text{m}/\text{year}$), and also supplies desirable information about the localization of the corrosion attack. An in depth understanding of the meaning of the localization factor used for evaluation of the resistance to pitting, is not yet at

hand, but the recorded localization factors of the order of 0.1 are believed to indicate a tendency to localized attack, but an inability to maintain the attack. Further work is needed to verify this expectation. An important step in this regard is the post-test examination of the copper electrodes used for the real-time monitoring after retrieval of LOT test parcel A2 early next year.

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