

## **Recorded corrosion rates on copper electrodes in the Prototype Repository at the Äspö HRL**

Bo Rosborg, Rosborg Consulting

April 2013

**Svensk Kärnbränslehantering AB**

Swedish Nuclear Fuel  
and Waste Management Co

Box 250, SE-101 24 Stockholm  
Phone +46 8 459 84 00



ISSN 1402-3091

SKB R-13-13

ID 1372807

# **Recorded corrosion rates on copper electrodes in the Prototype Repository at the Äspö HRL**

Bo Rosborg, Rosborg Consulting

April 2013

This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author. SKB may draw modified conclusions, based on additional literature sources and/or expert opinions.

A pdf version of this document can be downloaded from [www.skb.se](http://www.skb.se).

## Summary

Real-time corrosion monitoring by means of electrochemical methods has been applied in an effort to measure corrosion rates of pure copper in the Prototype Repository at the Äspö Hard Rock Laboratory. Copper electrodes were installed in bentonite blocks on top of the electrically heated copper canisters in two deposition holes (dh). Three nominally identical cylindrical copper electrodes were installed in dh 1 and another three in dh 5 a few days before the heat was turned on to the canisters in September 2001 and in May 2003 respectively. The temperature of the copper electrodes has been around 30°C in dh 1 and somewhat below 35°C in dh 5. Real-time corrosion monitoring<sup>1</sup> for both electrode set-ups was first applied in January 2004, and then periodically in 2005, 2006, 2008, and most recently in the end of 2010 just before work to open the outer section of the Prototype Repository was started.

The *recorded* corrosion rates fall below 1.3 µm/year (using a default value of n=2 in the software to convert the corrosion current density to a penetration rate by means of Faraday's law, and with no correction applied for the used measuring frequency of 0.01 Hz; also disregarding highly scattered data obtained for the copper electrodes in dh 1 during 2010). While the *recorded* rates on the electrodes in dh 5 first increased from about 0.2 µm/year in 2004 up to a maximum of 1.3 µm/year a year later (the drainage of the inner and outer sections was temporary closed in the end of 2004), and then gradually decreased to 0.7 µm/year in the end of 2010, the *recorded* rates on the electrodes in dh 1 show a quite different picture. The *recorded* rates fall in the range 0.4–0.7 µm/year and do not reflect any obvious decrease. However, it is anticipated that a similar time dependence as observed for the electrodes in dh 5 could have been present early on in the exposure; the electrodes were installed in 2001 but the first measurements were performed in 2004. Also, saturation of the bentonite in dh 1 may have been faster than in dh 5.

Since the major corrosion product formed on the copper electrodes is cuprite, it would have been more appropriate to use n=1 as a default value in the software to convert the corrosion current density to a penetration rate. Furthermore, electrochemical impedance spectroscopy on pure copper electrodes in Äspö groundwater open to air has shown that an applied measuring frequency of 0.01 Hz underestimates the polarization resistance with a factor of 4, and thus overestimates the corrosion rate with the same amount. Applying these corrections *better estimates* of the corrosion rates in 2010 fall below 0.4 µm/year. Assuming that the correction for the measuring frequency is correct this is the highest possible corrosion rate; the actual corrosion rate could in fact be lower due to parallel reduction-oxidation reactions.

The *estimated* corrosion rates on the copper electrodes in the Prototype Repository are lower than the rate estimated for the copper electrodes in LOT test parcel A2, about 0.4 compared to 0.8 µm/year after six years exposure respectively. Different operating conditions may be the reason for this. The average corrosion rate obtained from weight measurements of copper coupons in LOT test parcel A2 was found to be less than 0.5 µm/year, indicating that the real-time corrosion monitoring may provide conservative corrosion rates. Otherwise it just reflects variability in the near-field environment.

---

<sup>1</sup> SmartCET<sup>®</sup> corrosion monitoring systems were used. The equipment is today obtained from Honeywell Process Solutions, 2500 W. Union Hills Dr., Phoenix, AZ 85027, USA.

# Contents

|          |   |    |
|----------|---|----|
| <b>1</b> | <b>Introduction</b>   | 7  |
| 1.1      | The Prototype Repository  | 7  |
| 1.2      | The LOT test series   | 9  |
| <b>2</b> | <b>Brief account of applied techniques to measure corrosion rates</b> | 11 |
| 2.1      | Exposure of coupons   | 11 |
| 2.2      | Electrochemical methods   | 12 |
| 2.2.1    | The polarization resistance technique                                 | 12 |
| 2.2.2    | Harmonic distortion analysis  | 12 |
| 2.2.3    | Electrochemical impedance spectroscopy                                | 12 |
| 2.2.4    | Evaluation procedure  | 13 |
| 2.2.5    | Precautions   | 13 |
| 2.3      | Electrical resistance sensors   | 14 |
| <b>3</b> | <b>Experimental</b>   | 15 |
| 3.1      | The corrosion monitoring system                                       | 15 |
| 3.2      | The copper electrodes   | 16 |
| 3.2.1    | In the Prototype Repository   | 16 |
| 3.2.2    | In LOT test parcel A2   | 16 |
| 3.2.3    | In the bentonite test package   | 16 |
| 3.3      | Exposure  | 17 |
| 3.3.1    | The bentonite/saline groundwater environment                          | 17 |
| 3.3.2    | Start of exposure   | 18 |
| 3.3.3    | Redox conditions and environmental changes                            | 18 |
| 3.3.4    | Steady-state conditions   | 19 |
| <b>4</b> | <b>Results</b>  | 21 |
| 4.1      | From electrodes in dh 5   | 21 |
| 4.2      | From electrodes in dh 1   | 21 |
| <b>5</b> | <b>Discussion</b>   | 25 |
| 5.1      | Comparison of data from dh 1 and dh 5                                 | 25 |
| 5.2      | Comparison with other electrochemical data                            | 26 |
| 5.3      | Comparison with gravimetric data                                      | 27 |
| <b>6</b> | <b>Conclusions</b>  | 29 |
|          | <b>Acknowledgements</b>   | 30 |
|          | <b>References</b>   | 31 |
|          | <b>Appendix A</b> Acquired data from dh 1 during 2010                 | 33 |
|          | <b>Appendix B</b> Acquired data from dh 5 during 2010                 | 37 |

# 1 Introduction

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 bedrock – that is a KBS-3 repository (Rosborg and Werme 2008). 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. Besides rock movement, the biggest threat to the copper canister in the repository is corrosion.

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 (King et al. 2001) and updated in 2010 (King et al. 2010). Real-time monitoring of copper corrosion in actual or simulated repository environments is a further possibility to improve the basis to predict the corrosion behaviour of the copper canister.

The Äspö Hard Rock Laboratory (HRL) offers a realistic environment for different experiments and tests under the conditions that will prevail in a deep repository, see Figure 1-1. Complementary to exposure of components and coupons of copper, real-time corrosion monitoring of copper electrodes has been applied in two projects at the HRL, namely first in the LOT (acronym for “Long Term Test of Buffer Material” (Karnland et al. 2009)) test series (Rosborg et al. 2004a) and then in the Prototype Repository. During and after performance of real-time corrosion monitoring in LOT test parcel A2 starting in 2001, see Section 1.2, corrosion monitoring has in periods been performed on copper electrodes in two deposition holes (dh) of the Prototype Repository since January 2004 (Rosborg et al. 2004b). Furthermore, after retrieval of LOT test parcel A2, real-time corrosion monitoring has proceeded on the pre-exposed copper electrodes, and on later installed copper electrodes and sensors, in a bentonite test package that was made up of three bentonite rings from the retrieved test parcel (Rosborg and Pan 2008, Rosborg et al. 2011a).

## 1.1 The Prototype Repository

The Prototype Repository consists of a bored deposition tunnel with six full-scale canisters deposited in the same manner as in a future KBS-3 repository (Johannesson et al. 2004). It was divided in an inner section containing four and an outer section containing two canisters. The inner section was sealed during 2001 and the outer during 2003. 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, see Figure 1-2. The bentonite had been conditioned with tap water<sup>2</sup> to a water ratio of 17.5 % (Johannesson 2002). Three nominally identical copper electrodes were installed in the second upper bentonite block in dh 1 and in the upper block in dh 5, thus above the canisters, a few days before the heat was turned on to the canisters on 2001-09-17 and 2003-05-08 respectively.

Work to open the outer section of the Prototype Repository started in November 2010 and the two canisters in the outer section were retrieved during 2011. Before the canister in dh 5 was retrieved a bentonite block containing the copper electrodes was removed by a stitch drilling and bending procedure for post-test examination (Rosborg 2013a).

---

<sup>2</sup> Bicarbonate containing tap water from the municipality of Lidköping with a very low chloride ion content.

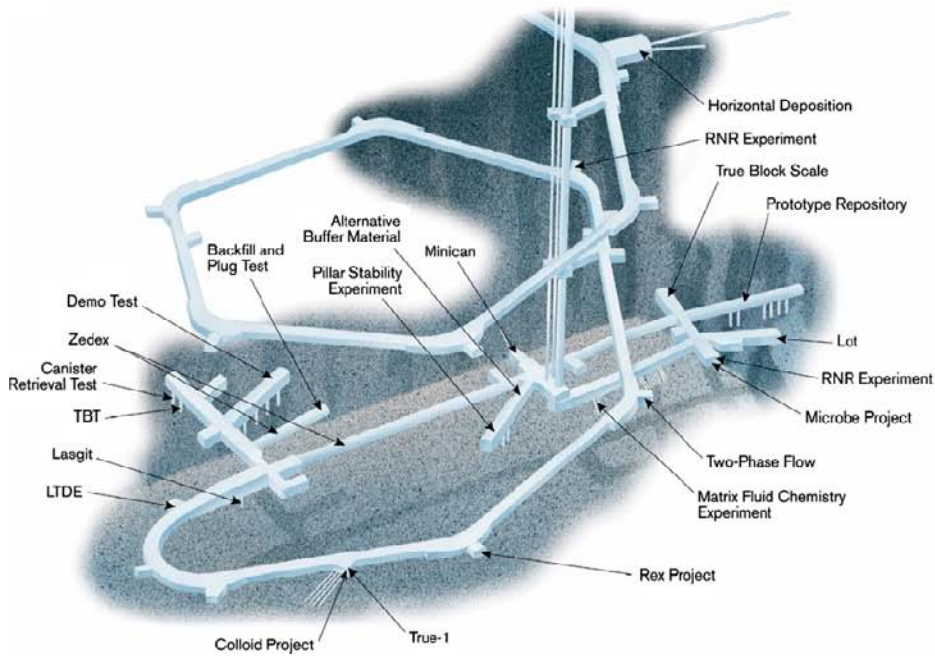
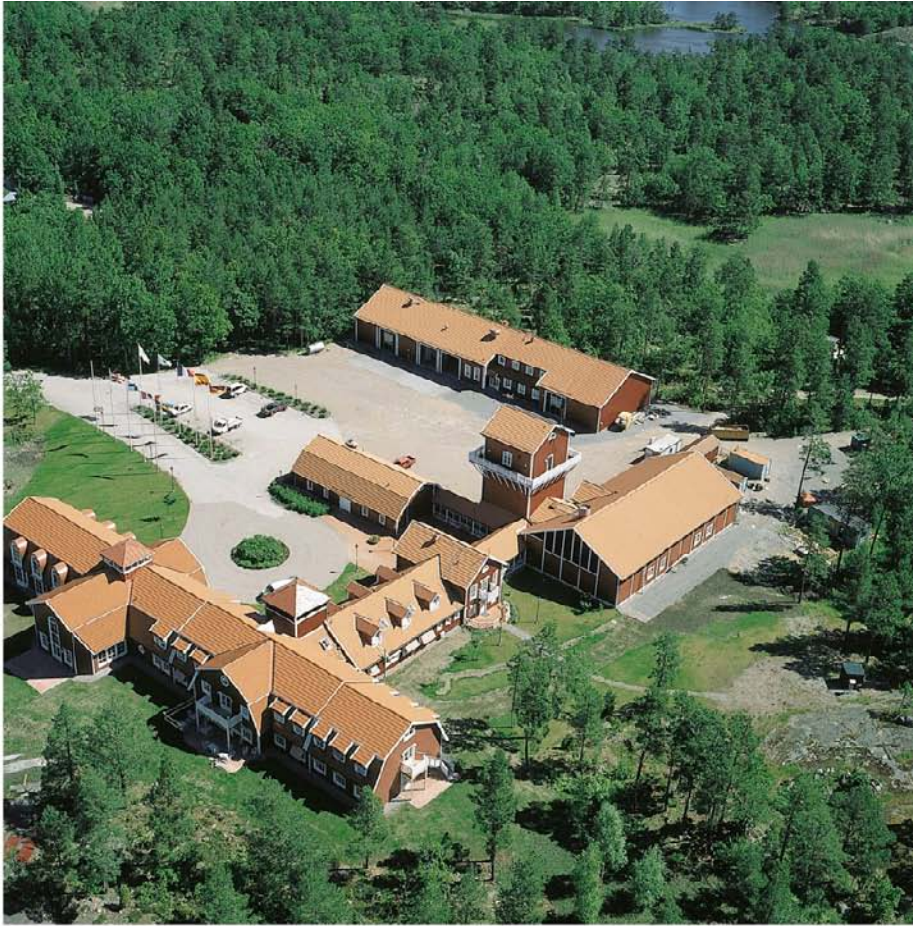
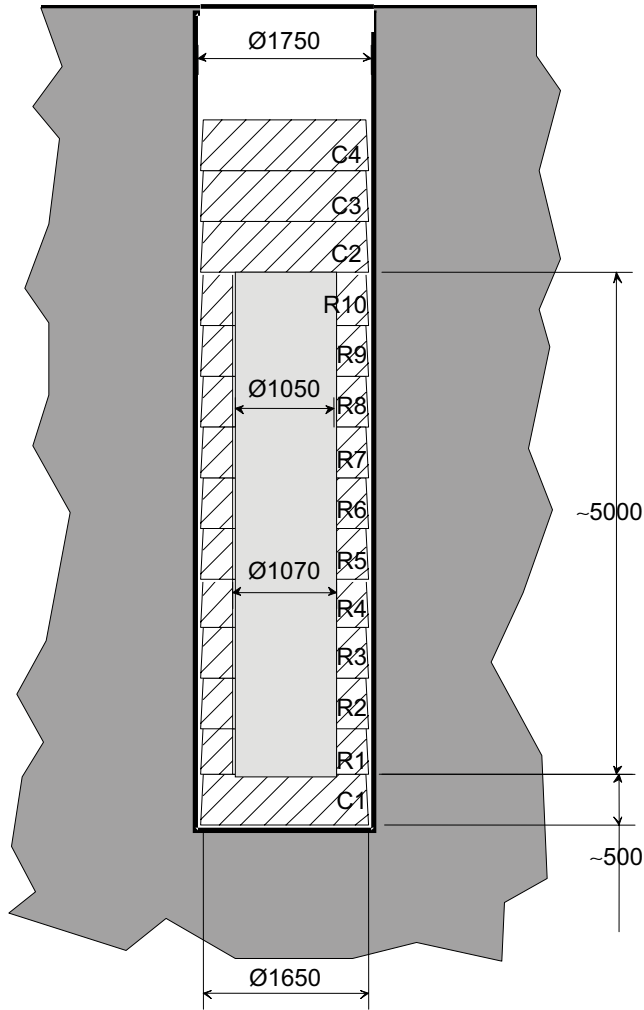


Figure I-1. The Åspö Hard Rock Laboratory above and below ground.



*Figure 1-2. A canister in its deposition hole surrounded by bentonite rings and blocks.*

## 1.2 The LOT test series

The LOT test series was initiated with conditions similar to those in a final KBS-3 repository with bentonite rings of smaller dimensions (Karlund et al. 2009). The main purpose is to study the mineralogical stability and behaviour of the bentonite clay. Each test parcel contains forty prefabricated bentonite rings placed on top of each other around a central copper tube (with bentonite ring 1 in the bottom and bentonite ring 40 in the top), and contains copper coupons in bentonite rings 22 and 30. The test parcels were placed in 4 m deep holes in the granitic rock. In addition to exposure of copper coupons a set of three nominally identical cylindrical copper electrodes were also installed in bentonite ring 36 of LOT test parcel A2 to make it possible to perform real-time corrosion monitoring by means of electrochemical methods (Rosborg et al. 2004a). The test parcel was emplaced on 1999-10-29.

## 2 Brief account of applied techniques to measure corrosion rates

Exposure of coupons (and components) and SmartCET<sup>®</sup> real-time corrosion monitoring have been used for in situ corrosion testing of copper in the Äspö HRL. After retrieval of LOT test parcel A2 also a few other methods have been applied for the continued corrosion monitoring in the bentonite test package. This has been done to facilitate interpretation of results obtained from the in situ testing at Äspö and to gain further information about the corrosion behaviour of copper in a bentonite/saline groundwater environment.

Below a brief account of the applied techniques to measure corrosion rates of copper under free corrosion is given. One desirable method for measuring low corrosion rates is conspicuous by its absence, that is the quartz crystal micro-balance method. It is unfortunately limited to measurements in gases and liquids, and could thus not be used in the environment of current interest.

### 2.1 Exposure of coupons

Exposure of coupons supply information about the average corrosion rate and the corrosion behaviour. The average corrosion rate is estimated by weighing a coupon before and after exposure, the latter after proper cleaning and removal of the corrosion products on the coupon. A post-test examination of the coupon is performed to find out the nature of the corrosion attack and the formed corrosion products.

The appearance of a copper coupon after exposure in a LOT test parcel is exemplified in Figure 2-1. Dominating corrosion product was cuprite,  $\text{Cu}_2\text{O}$ , and paratacamite,  $\text{Cu}_2(\text{OH})_3\text{Cl}$ , was found here and there on top of the cuprite. In LOT test parcel 2 the average corrosion rate was estimated to fall below  $0.5 \mu\text{m}/\text{year}$  (Karnland et al. 2009).



*Figure 2-1. Appearance of a copper coupon after exposure in the Äspö HRL.*



## 2.2 Electrochemical methods

The SmartCET<sup>®</sup> corrosion monitoring system which has been used at Äspö operates in a multi-technique mode, applying electrochemical noise, harmonic distortion analysis, polarization resistance, and solution resistance measurements. In the bentonite test package also other electrochemical methods have been used. Electrochemical impedance spectroscopy (EIS) has for instance been used to estimate the corrosion rate of installed electrical resistance (ER) sensors (Rosborg et al. 2011a). Below only applied techniques to measure corrosion rates are considered.

### 2.2.1 The polarization resistance technique

In a polarization resistance measurement the electrode is forced slightly from its corrosion potential, usually by a potential disturbance, and from the current response the so-called polarization resistance (the slope of the potential – current density curve at the corrosion potential) can be estimated (Scully 2000, 2003, ASTM G96 – 90(2008)). Knowing the polarization resistance, the corrosion current density can then be calculated and converted to a penetration rate by means of 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. 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.

The corrosion rate expressed as a corrosion current density is calculated from the measured polarization resistance using the so-called Stern-Geary equation, and the corrosion rate expressed as a penetration rate is then calculated from the corrosion current density using Faraday's law, see Section 2.2.4.

### 2.2.2 Harmonic distortion analysis

Harmonic distortion analysis relies on the non-linear nature of electrochemistry (Darowicki and Majewska 1999, Cottis 2008). An electrochemical system (electrode in an electrolyte), in this case the cylindrical copper electrodes installed in a bentonite block, is not completely linear but more or less non-linear. When applying harmonic distortion analysis the current answer after a potential disturbance is not only measured at the same frequency but also for multiples of this frequency. Both the corrosion current density and the Tafel-constants, and the B-value, can thus be determined.

### 2.2.3 Electrochemical impedance spectroscopy

When performing EIS measurements an alternating voltage (or current) signal is applied to the electrode and the resulting current (or voltage) response is measured for different frequencies of the applied signal (Cottis and Turgoose 1999). From the voltage and current signals the complex impedance is calculated for the applied frequencies. The result is usually presented in a Bode or a Nyquist plot: In a Bode plot the absolute value of the impedance (modulus of impedance) and the phase angle is plotted versus the logarithm of the applied frequency. In a Nyquist plot the imaginary part of the impedance is plotted versus the real part.

The polarization resistance can be obtained from fitting of the impedance data to equivalent circuits as described in Cottis and Turgoose (1999).

EIS is a very versatile method that supplies information both about corrosion mechanisms and rates.

## 2.2.4 Evaluation procedure

The different steps to calculate a corrosion rate from electrochemical data expressed as a penetration rate is described below.

**The corrosion current density** – The corrosion rate expressed as a corrosion current density is calculated from the measured polarization resistance using the Stern-Geary equation (Stern and Geary 1957, ASTM G102 – 89(2010))

$$i_{corr} = \frac{B}{R_p}$$

where  $i_{corr}$  is the corrosion current density in  $A/cm^2$ ,  $B$  the so-called Stern-Geary coefficient (also called the B-value) in  $V$ , and  $R_p$  the polarization resistance in  $ohm \cdot cm^2$ . The theory behind this equation is presented in most text books in corrosion. Thus, to be able to calculate the corrosion current density, one has to know not only the polarization resistance but also the B-value. The latter is not a constant, but needs to be determined separately for the actual application, or can more or less arbitrarily be chosen based on experience. (Certain commercially available instruments for polarization resistance measurements use a pre-selected value, such as 30 mV, which based on experience may give adequate accuracy in many cases, however, be quite misleading in others.) The SmartCET® corrosion monitoring system measures the B-value by means of harmonic distortion analysis.

**Penetration rate** – The corrosion rate expressed as a penetration rate is calculated from the corrosion current density using Faraday's law as

$$CR = 3.27 \frac{i_{corr} W}{d n}$$

where  $CR$  is the corrosion rate in  $\mu m/year$ ,  $i_{corr}$  the corrosion current density in  $\mu A/cm^2$ ,  $d$  the density in  $g/cm^3$ ,  $W$  the atomic weight (dimensionless), and  $n$  the number of electrons transferred to oxidize an atom. For pure copper  $d=8.94 g/cm^3$  and  $W= 63.54$  and consequently the corrosion rate for copper in  $\mu m/year$  can be written as

$$CR = 23.3 \frac{i_{corr}}{n}$$

Thus, in order to calculate the corrosion rate as a penetration rate knowledge is needed about which kind of corrosion products that are formed, and in what relative amounts. If only univalent corrosion products are formed, for instance  $Cu_2O$ , or only divalent, for instance  $CuO$ ,  $n=1$  and  $n=2$  respectively should be used. If both uni- and divalent corrosion products are formed, a mean value between these extremes can be used that reflects the amount of corrosion products of the different types. A post-test examination of exposed electrodes is needed to find out the actual conditions.

## 2.2.5 Precautions

Here some general precautions and requirements for the electrochemical methods are briefly considered (Scully 2003, Cottis and Turgoose 1999).

**The Stern-Geary equation** is used to calculate the corrosion current density from the measured polarization resistance. Strictly it is based on activation control only. However, it is also applied for electrochemical systems with mass-transfer limitations.

The presence of **parallel reduction-oxidation (redox) reactions** will cause an overestimation of the corrosion rate. In such a case the corrosion of the metal or alloy constitutes only a fraction of the recorded current.

**Steady-state conditions** for the corroding system are necessary for the above electrochemical methods to supply reliable data. The corrosion potential has to be quite stable and not change significantly during a measurement. This requirement is fulfilled in the present work. Even if the corrosion potential for practical reasons has not been followed during the exposure, the stability of the obtained data is a proof of steady-state conditions. (This is no surprise since the copper electrodes were installed in the bentonite blocks long before the measurements started.)

The corrosion rate may be underestimated if **the solution resistance** is sizeable and proper corrections for the solution resistance is not made.

**The voltage perturbation amplitude** should be kept small enough not to cause changes of the corroding metal and a drift of the corrosion potential.

**The voltage perturbation frequency** needs to be sufficiently low to measure the true polarization resistance. A too high measuring frequency underestimates the polarization resistance, and thus overestimates the corrosion rate. However, for practical reasons (to shorten time of measurement) a higher measuring frequency may be used, which will then require that the *recorded* data are later corrected based on supporting measurements to get a *better estimate*. This procedure has been applied in the present work (Rosborg et al. 2004a).

## 2.3 Electrical resistance sensors

ER measurements to estimate the corrosion rate of a metal are based on the fact that a decrease in thickness of a metallic conductor causes an increase in electrical resistance (ASTM G96 – 90(2008), Brossia 2008). The sensitivity of an ER sensor is defined by its thickness, however, a lower thickness also means a shorter service life of the sensor; thus, a compromise between sensitivity and sensor life is needed. ER sensors generally do not distinguish between general and localized corrosion forms. A post-test examination is required to reveal the corrosion attack and verify the results.

## 3 Experimental

This section contains information about the used real-time corrosion monitoring system, the copper electrodes, and the exposure conditions.

### 3.1 The corrosion monitoring system

The used SmartCET<sup>®</sup> corrosion monitoring system operates in a multi-technique mode<sup>3</sup>, 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 (Cottis 2008, Cottis and Turgoose 1999). Electrochemical noise data is taken at a frequency of one reading per second. This technique has earlier been found to overestimate the corrosion rate of copper in a bentonite/saline groundwater environment and has been disregarded in the following (Rosborg et al. 2005).

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  $\pm 25$  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 is required to calculate the corrosion rate from the recorded polarization resistance data using the Stern-Geary relationship. 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 used voltage perturbation frequency of 0.01 Hz is too high for measurement of the very low corrosion rates of interest (Rosborg et al. 2004a). 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 have been used (ignoring practical problems), but it was decided to stay with the present instrumental set-up and instead correct recorded values afterwards. An interdependence exists between requirements for steady-state conditions, the amplitude of the voltage signal, and lowering of the measuring frequency.

When using a SmartCET<sup>®</sup> corrosion monitoring system certain values are fed into the software in advance, including the anticipated B- and n-values. From start of measurements on the copper electrodes in LOT test parcel A2 a default value of  $B=10.3 \text{ mV}^4$  was used and has for practical reasons been kept since then. It was based on earlier findings from a similar material-environment system. A default value of  $n=2$  was used for conversion of the corrosion current density to corrosion (penetration) rate using Faraday's law. These values are afterwards corrected; the actual B-value is obtained from the harmonic distortion analysis, and a proper n-value from knowing the kind and amount of the corrosion products formed (ASTM G102 – 89(2010)). (If  $n=1$  had been used as a default value the recorded data should be doubled.)

Two SmartCET<sup>®</sup> corrosion monitoring units have been used for measurements on the copper electrodes in the Prototype Repository: (i) a one-channel Äspö unit, and (ii) a two-channels KTH lab unit. When the Äspö unit was used, the measurements on the copper electrodes in dh 1 and dh 5 were performed in turns after each other.

<sup>3</sup> SmartCET<sup>®</sup> Technology – User Guide v06 04 03, InterCorr International, Houston, TX.

<sup>4</sup> Private communication from A Brennenstuhl, Kinetics Inc, Toronto, Canada, to G Quirk, May 2001.

## 3.2 The copper electrodes

The copper canisters are manufactured from pure oxygen-free copper (99.99 % Cu) with a deliberate addition of approximately 50 ppm phosphorous to improve creep properties (Werme 1998). The cylindrical copper electrodes and rectangular coupons used for the in situ testing at Äspö were manufactured from actual canister material.

### 3.2.1 In the Prototype Repository

Three nominally identical cylindrical copper electrodes were installed in dh 1 and another three in dh 5 a few days before the heat was turned on to the canisters on 2001-09-17 and 2003-05-08 respectively. The electrodes have the dimensions  $\text{Ø}60 \times 100$  mm and a nominal surface area of about  $232 \text{ cm}^2$  each. The copper electrodes in dh 1 were installed in the second upper bentonite block (C3) and the electrodes in dh 5 in the upper bentonite block (C4), see Figure 1-2.  $\text{Ø}60$  mm holes were first drilled in the bentonite blocks to a depth of 250 mm, the electrodes were placed in the holes after which the holes were refilled with bentonite powder.

The temperature readings in the second upper bentonite block (C3) with the copper electrodes in dh 1 fall in the range  $29\text{--}36^\circ\text{C}$  during the real-time corrosion monitoring and has for the last few years been around  $30^\circ\text{C}$ . Ditto in the upper bentonite block (C4) in dh 5 has most of the time been somewhat below  $35^\circ\text{C}$ .

### 3.2.2 In LOT test parcel A2

The three cylindrical copper electrodes for real-time corrosion monitoring in LOT test parcel A2, each of  $98.7 \text{ cm}^2$  surface area, were installed in bentonite ring 36 of the test parcel (Rosborg et al. 2004a). The electrodes were positioned near the top of the test parcel, where the temperature was about  $24^\circ\text{C}$ .

### 3.2.3 In the bentonite test package

After retrieval of LOT test parcel A2 from the Äspö HRL in January 2006, 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 (Rosborg and Pan 2008). After retrieval the conditions for the pre-exposed copper electrodes in the bentonite test package were 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.

During 2006 new copper electrodes were installed in the test package. In January 2007 four  $35 \text{ }\mu\text{m}$  thick ER sensors of ZAG<sup>5</sup> design, and made of pure copper, were also installed in the bentonite test package (Rosborg et al. 2011b, Rosborg et al. 2013b). ER measurements have then been performed up to April 2011, when the bentonite test package was cut in pieces for post-test examination of electrodes and sensors.

---

<sup>5</sup> Slovenian National Building and Civil Engineering Institute, Dimičeva 12, SI – 1000 Ljubljana, Slovenia.

### 3.3 Exposure

Following some general information about the bentonite/saline groundwater environment, the start of exposure of copper samples and the observed and anticipated environmental changes are briefly discussed.

#### 3.3.1 The bentonite/saline groundwater 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. After the oxygen has been consumed in the repository corrosion will be controlled completely by the supply of dissolved sulphide to the canister.

The main mineral constituent in bentonite clay is montmorillonite, which has a sheet-like crystal structure (Karnland et al. 2006). Wyoming bentonite used in the present work and sold under the commercial name MX-80 is dominated by natural sodium montmorillonite clay (about 80 % by weight), which is responsible for the desired physical properties. Accessory minerals are quartz, tridymite, cristobalite, feldspars, muscovite/illite, sulphides, and small amounts of other minerals and organic carbon.

The cation exchange capacity is around 0.8 eq/kg bulk material. The natural exchangeable cations are sodium, calcium, magnesium and small amounts of potassium. The specific surface area is around 550 m<sup>2</sup>/g material and the grain density is around 2,750 kg/m<sup>3</sup>.

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) (King et al. 2010, Laaksoharju et al. 1998). The chloride concentration in the groundwater can vary within very wide limits, ranging from 5 mg/dm<sup>3</sup> to 50 g/dm<sup>3</sup>. Groundwater analyses from different parts of Sweden show sulphide concentrations ranging from <0.01 mg/dm<sup>3</sup> up to 1 mg/dm<sup>3</sup>, with 0.1 mg/dm<sup>3</sup> 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.

Table 3-1 shows a typical composition of the groundwater in the Äspö HRL.

**Table 3-1. Groundwater composition from the Äspö Hard Rock Laboratory.**

| Ion                           | mM                             | mg/dm <sup>3</sup> |
|-------------------------------|--------------------------------|--------------------|
| Na <sup>+</sup>               | 100                            | 2,300              |
| K <sup>+</sup>                | 0.28                           | 11                 |
| Ca <sup>2+</sup>              | 47.3                           | 1,896              |
| Mg <sup>2+</sup>              | 2.4                            | 58                 |
| Cl <sup>-</sup>               | 178                            | 6,311              |
| HCO <sub>3</sub> <sup>-</sup> | 0.44                           | 27                 |
| SO <sub>4</sub> <sup>2-</sup> | 4.6                            | 442                |
| HS <sup>-</sup>               | 0.005                          | 0.15               |
| pH 6.9±0.1                    | E <sub>redox</sub> –308 mV SHE |                    |

### 3.3.2 Start of exposure

In a “simple” corrosion test start of exposure is obvious; it happens when the sample is placed in the solution, or alternatively when the solution has been poured into the test vessel. It is far more complicated to define start of exposure when exposing a copper sample in a bentonite/saline groundwater environment. Here bentonite rings and blocks are first prefabricated and conditioned (thus containing a certain amount of pore water before installing the copper samples), then space for the copper coupons and electrodes are machined, and before or after installing the bentonite rings and blocks in the test positions the coupons and electrodes are placed in these. Later heat may be turned on and the bentonite is heated. The surrounding groundwater reaches the outer surface of the bentonite rings and blocks and cause swelling of the bentonite. After a considerable length of time amounting to years a steady-state is reached where the pore water facing the copper samples has established a steady-state with the groundwater.

The chemical environment in the electrode/bentonite interface is determined by the composition of the bentonite pore water. From start of exposure in the present case it was dominated by bicarbonate containing tap water. Later on the pore water will be determined by the interaction between the bentonite and the saline groundwater in the surrounding rock.

Thus, start of exposure of a corrosion test in a bentonite/saline groundwater environment is quite complicated. Average corrosion rates obtained from copper coupons can either be calculated using the entire exposure time from emplacement of the test object, or alternatively from the time when heat has been turned on, or otherwise.

Real-time corrosion monitoring supplies the corrosion rate when the measurement is performed, however, if a recorded rate should represent steady-state conditions, such a steady-state has of course first to be established.

### 3.3.3 Redox conditions and environmental changes

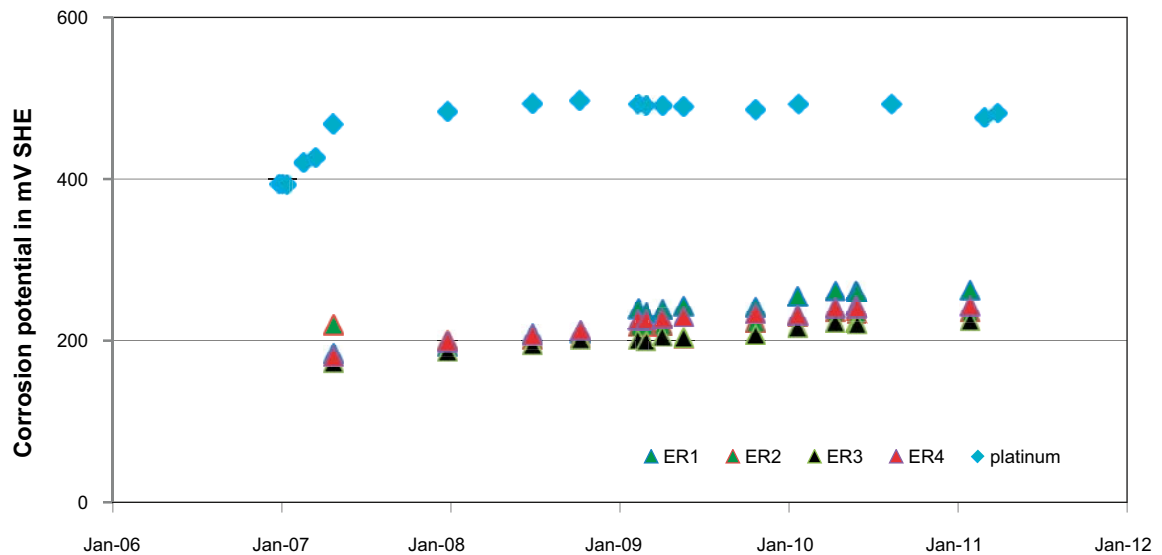
Initially after installation of samples and test parcels oxic conditions prevail and are expected to last for a considerable time amounting to years, however, after a long time anoxic conditions are anticipated.

The corrosion potential of the electrodes in the Prototype Repository and LOT test parcel A2 has not been followed due to experimental difficulties. The corrosion potential of the copper electrodes in dh 5 has, however, been measured immediately after part of the concrete plug to the outer section was removed (Rosborg 2013a). The corrosion potentials for the three copper electrodes fell in the range  $-60$  to  $-30$  mV SHE. Thus, the near-field environment seemed to be mildly oxidising still after seven years exposure.

The corrosion potential of the electrodes in the *bentonite test package* has been followed from retrieval of LOT test parcel A2 to end of exposure in April 2011 and verified that oxic conditions existed all through the testing (Rosborg et al. 2013b). This is exemplified by the corrosion potentials for the ER sensors (and the electrode potential of platinum) shown in Figure 3-1. The cylindrical copper electrodes of canister quality had somewhat lower corrosion potentials in the range  $157$ – $206$  mV SHE during 2010.

It is anticipated that the copper electrodes in the Prototype Repository have experienced similar corrosion potentials earlier during their exposure. Blue-green corrosion products were also found on the examined copper electrode from dh 5, verifying that the electrode had reached a corrosion potential allowing Cu(II) corrosion products to be formed (Rosborg 2013a).

During operation of the Prototype Repository the drainage to the inner and outer sections have temporarily been closed once. In early November 2004 it was closed and reopened about a month later. About three weeks after the closure an obvious increase in pressure from the installed total and pore pressure gauges in the bentonite was noticed.



**Figure 3-1.** Evolution of the corrosion potential with time for the ER sensors exposed in the bentonite test package.

### 3.3.4 Steady-state conditions

Even if the corrosion potentials of the copper samples have changed during the exposure in the Äspö HRL, the changes have been so slow that from a corrosion monitoring point of view steady-state conditions have prevailed during the monitoring periods. The steady-state conditions in the Prototype Repository and LOT test parcel A2 are manifested by the slow change of the *recorded* corrosion rates, see Sections 4.1 and 4.2.

That steady-state conditions have prevailed in the *bentonite test package* are obvious from Figure 3-1 (Rosborg et al. 2013b).



## 4 Results

Below the *recorded* corrosion rates<sup>6</sup> from the SmartCET<sup>®</sup> corrosion monitoring on the copper electrodes in dh 1 and dh 5 are first presented using a default value of  $n=2$  when converting the corrosion current density to a penetration rate by means of Faraday's law. Also, any correction for the used measuring frequency has not been applied. To get a better estimate of the actual rates the recorded values should be multiplied with 2 (since the most abundant corrosion product cuprite is univalent) and divided by a factor of 4 to correct for the used measuring frequency (Rosborg et al. 2004a); to get an even better estimate, a balanced "valance value" could be used instead of  $n=1$  when the post-test examination of the electrodes has revealed the relative amounts of corrosion products of valence 1 and 2.

The *recorded* current reflects so to say the overall electrochemical activity on the electrode and not necessarily only that valid for corrosion of copper; the actual corrosion rates could be lower due to the presence of other redox couples, however, they could not be bigger than the recorded values.

Since the results obtained from dh 1 give a more complex picture, the results from dh 5 are presented first. Examples of acquired primary data are presented in Appendices A and B.

### 4.1 From electrodes in dh 5

The *recorded* corrosion rate on the copper electrodes in dh 5 during part of 2010, and its change with time, is seen in Figure 4-1. It is of the order of  $0.7 \mu\text{m}/\text{year}$  and slightly decreasing (ignoring the temporary increase in early November).

Data from 2004 through 2010 are compiled in Figure 4-2. The *recorded* corrosion rate has first increased from quite low values of the order of  $0.2 \mu\text{m}/\text{year}$  up to a maximum of  $1.3 \mu\text{m}/\text{year}$  during 2005, and then gradually decreased to the value given above. (Even if the corrosion rate has not been recorded continuously from 2005 up to 2010, it is reasonable to assume that gradually decreasing values have dominated the period.)

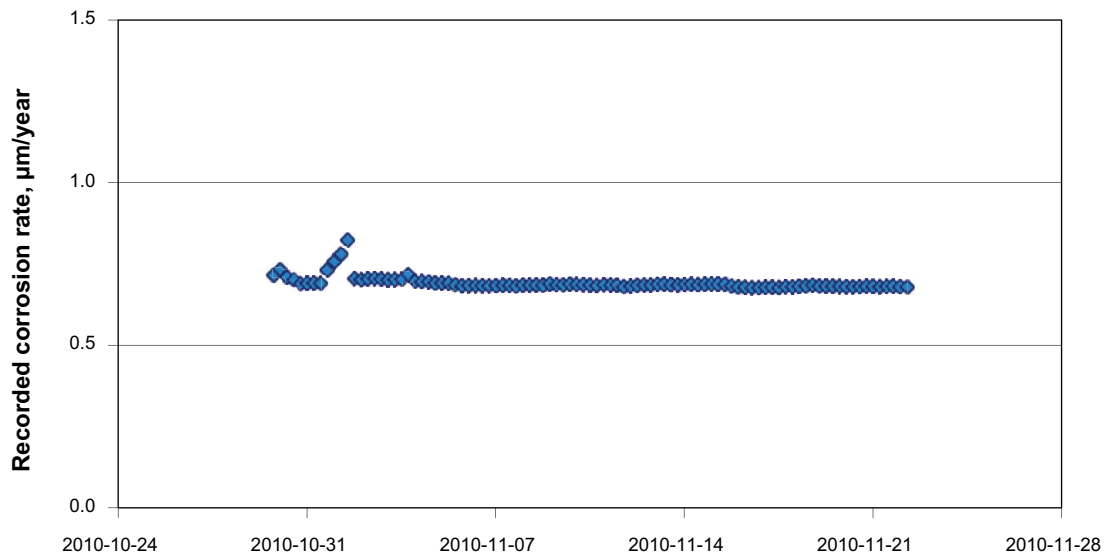
The drastic change of the *recorded* corrosion rate between 2004 and 2005 is explained by a closure of the drainage to the inner and outer section of the Prototype Repository in November 2004. About three weeks after the closure an obvious increase in pressure from the installed total and pore pressure gauges was noticed; the drainage was reopened a month after the temporary closure. It is assumed that the near-field environment from now on is dominated by the saline groundwater in the surrounding rock rather than by the tap water from the manufacturing of the bentonite (Rosborg 2013a).

### 4.2 From electrodes in dh 1

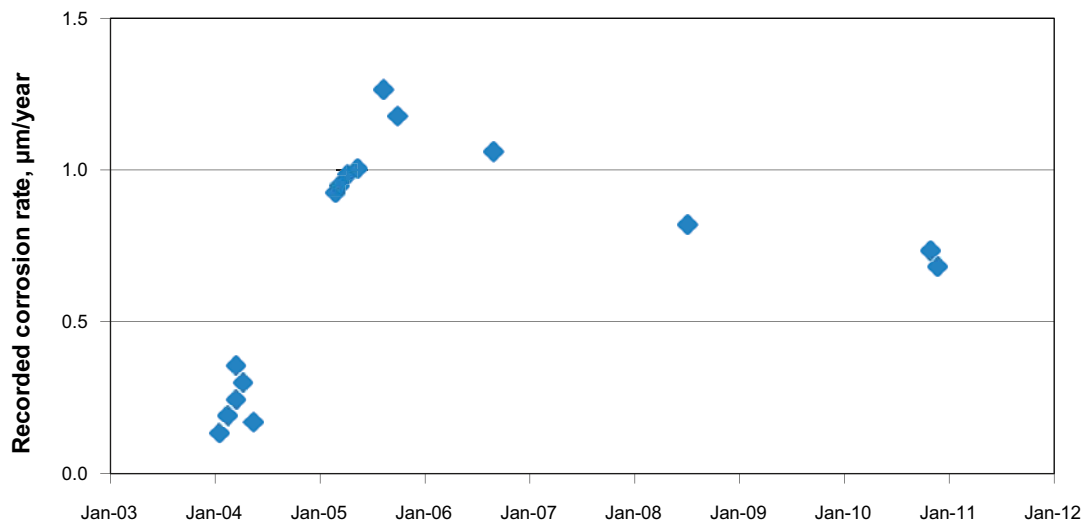
*Recorded* corrosion rates for the copper electrodes in dh 1 from 2008 and 2010 are shown in Figures 4-3a and 4-3b respectively, and *recorded* data from 2004 through 2010 are compiled in Figure 4-4. While the *recorded* rates from the measuring periods during 2008 and earlier show about the same values, the *recorded* rates during 2010 show quite a different result with a great scatter. The *recorded* rates seem to belong to two populations, marked with red and blue respectively in Figure 4-3b, one of which fits earlier obtained data (showing the same electrochemical characteristics) and another showing both higher *recorded* rates and a large scatter (with quite different characteristics, and besides the high scatter also considerable differences in magnitude between the anodic and cathodic Tafel coefficients; the periods with a small spread show low *recorded* corrosion rates and similar anodic and cathodic Tafel coefficients in agreement with results from measurements during both 2008 and earlier). The former data does not reveal this behaviour, thus it is anticipated that the source of the scattered data is experimental deficiencies of some kind.

---

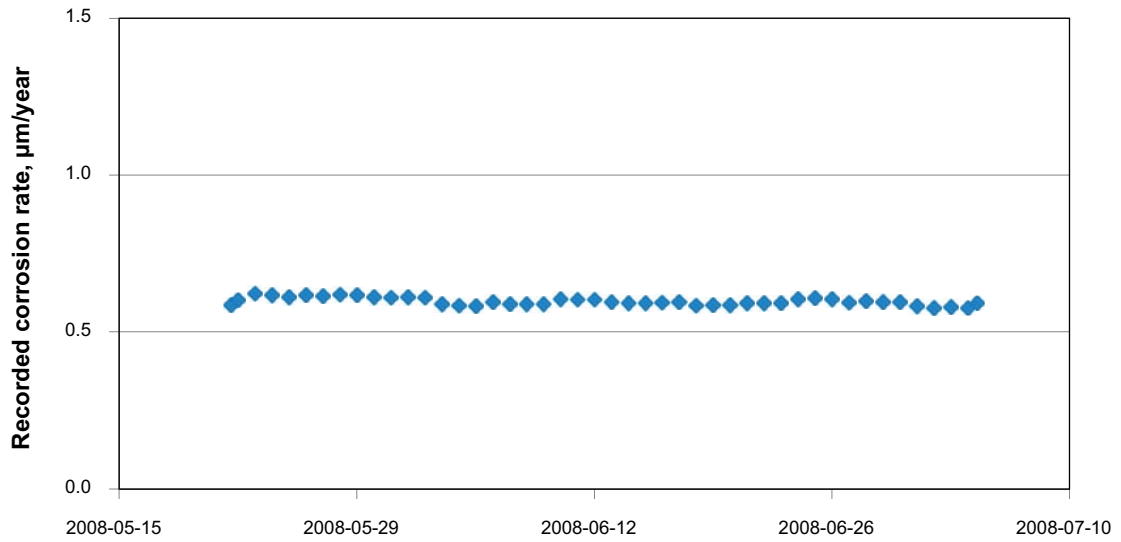
<sup>6</sup> The measured B-value has been applied in place of the default value  $B=10.3 \text{ mV}$ .



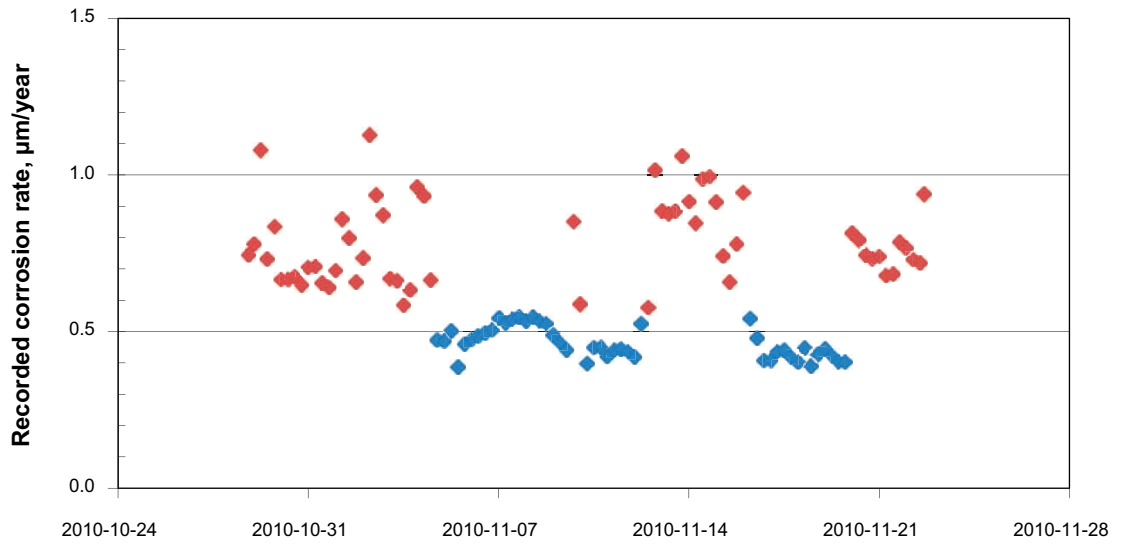
**Figure 4-1.** Recorded corrosion rates ( $n=2$  and 0.01 Hz) for the copper electrodes in deposition hole 5 of the Prototype Repository during 2010.



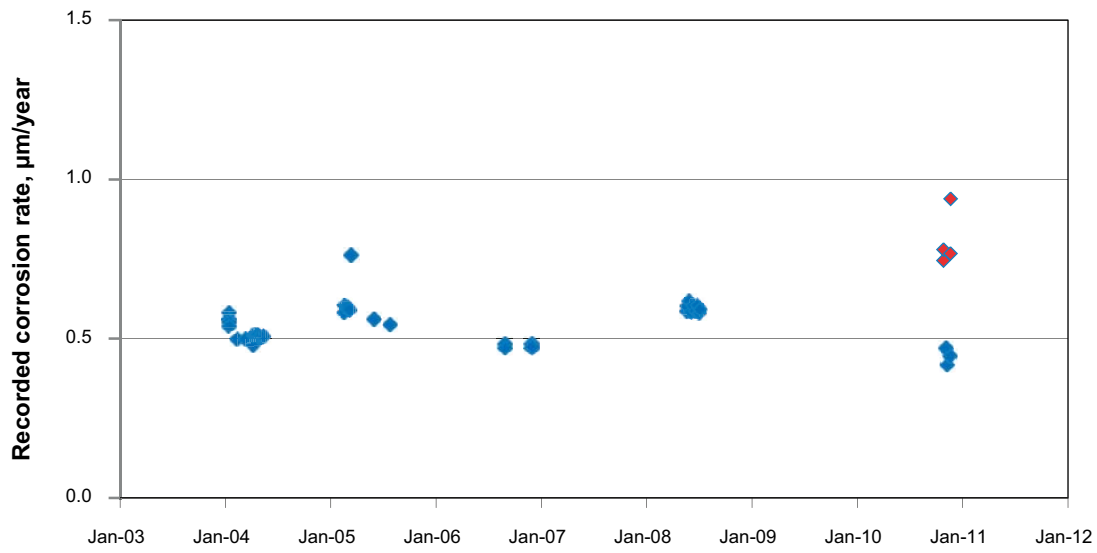
**Figure 4-2.** Recorded corrosion rates ( $n=2$  and 0.01 Hz) for the copper electrodes in deposition hole 5 of the Prototype Repository since 2004.



**Figure 4-3a.** Recorded corrosion rates ( $n=2$  and 0.01 Hz) for the copper electrodes in deposition hole 1 of the Prototype Repository during 2008.



**Figure 4-3b.** Recorded corrosion rates ( $n=2$  and 0.01 Hz) for the copper electrodes in deposition hole 1 of the Prototype Repository during 2010.



*Figure 4-4. Recorded corrosion rates ( $n=2$  and 0.01 Hz) for the copper electrodes in deposition hole 1 of the Prototype Repository since 2004.*

## 5 Discussion

In the following the corrosion rates from the real-time corrosion monitoring on the copper electrodes in dh 1 and dh 5 will first be compared with each other and related to information from operation of the Prototype Repository, then compared with data obtained from electrochemical measurements on the electrodes in LOT test parcel A2 and the bentonite test package, and finally compared with gravimetric data obtained from exposure of copper coupons in LOT test parcels and from electric resistance measurements on copper sensors in the bentonite test package.

In Figures 4-1 through 4-4 *recorded* corrosion rates are shown. Since the major corrosion product formed is cuprite, it is more relevant to use  $n=1$  in Faraday's law to convert the corrosion current density to a penetration rate. Furthermore, EIS on pure copper electrodes in Äspö groundwater open to air has shown that an applied measuring frequency of 0.01 Hz underestimates the polarization resistance with a factor of 4, and thus overestimates the corrosion rate with the same amount (Rosborg et al. 2004a). These corrections have been applied below. Assuming that the correction for the measuring frequency is correct the new *estimates* of the corrosion rate is the highest possible corrosion rate. The actual corrosion rate could in fact be lower due to parallel redox reactions.

### 5.1 Comparison of data from dh 1 and dh 5

The *recorded* corrosion rates on the copper electrodes in dh 1 and dh 5 fall below  $1.3 \mu\text{m}/\text{year}$  (using a default value of  $n=2$  in the software, and with no correction applied for the used measuring frequency of 0.01 Hz; also disregarding the highly scattered data obtained for the copper electrodes in dh 1 during 2010).

The *recorded* corrosion rates for the electrodes in dh 5 first increased from about  $0.2 \mu\text{m}/\text{year}$  in 2004 up to a maximum of  $1.3 \mu\text{m}/\text{year}$  a year later and then gradually decreased to  $0.7 \mu\text{m}/\text{year}$  in the end of 2010. The drainage of the inner and outer sections was temporarily closed in the end of 2004, and it is anticipated that the near-field environment before then was dominated by the tap water and from 2005 on so to say dominated by the saline groundwater in the surrounding rock rather than by the bicarbonate containing tap water (Rosborg, 2013a).

The *recorded* rates on the electrodes in dh 1 show a quite different picture. The *recorded* corrosion rates fall in the range  $0.4\text{--}0.7 \mu\text{m}/\text{year}$  and do not reflect any obvious decrease. However, it is anticipated that a similar time dependence as observed for the electrodes in dh 5 could have been present early on in the exposure; the electrodes were installed in 2001, but the first measurements were performed in 2004. Also, saturation of the bentonite in dh 1 may have been faster than in dh 5.

In Table 5-1 *better estimates* of the corrosion rates are given (with corrections for the applied measuring frequency and using  $n=1$  in Faraday's law, thus ignoring the amount of divalent corrosion products formed. However, since cuprite is the dominant corrosion product this will only result in a minor overestimation of the corrosion rates.) These values are used for comparison with other data below.

**Table 5-1. Better estimates of the corrosion rates for the copper electrodes in dh 1 and dh 5 in the end of 2010.**

| Position | Installed | Retrieved | Exposure years | Temperature °C | Corrosion rate $\mu\text{m}/\text{year}$ |
|----------|-----------|-----------|----------------|----------------|--|
| PR dh 1  | 2001      |           | 9              | 30             | 0.3                                      |
| PR dh 5  | 2003      | 2011      | 7              | 35             | 0.4                                      |

## 5.2 Comparison with other electrochemical data

In Table 5-2 the *estimated* final corrosion rates for the copper electrodes in dh 1 and dh 5 are compared to corresponding rates for copper electrodes exposed in LOT test parcel A2 at Äspö and later in the retrieved bentonite test package.

The final corrosion rates on the copper electrodes that were first exposed in LOT test parcel A2 at Äspö (LOT A2 in the table) and then after retrieval of the test parcel also in the bentonite test package (btp pre-exposed in the table) are higher than the rates for the copper electrodes in the Prototype Repository. However, the copper electrodes installed in the bentonite test package during 2006 (btp new) show somewhat lower final corrosion rates for yet unknown reasons. Different operating conditions may be the reason for this. (The same SmartCET<sup>®</sup> corrosion monitoring system was used for these real-time measurements.)

The *estimated* final corrosion rates obtained from EIS measurements on electric resistance (ER) sensors exposed in the bentonite test package (with corrosion potentials shown in Figure 3-1), and which survived the test period of 4 years, are also included in the table (Rosborg et al. 2013b).

Even if some unexplained differences exist between the data, in particular the higher rates observed for the pre-exposed copper electrodes, the *estimated* final corrosion rates after extended exposure are all well below 1 µm/year.

**Table 5-2. Comparison with estimated final corrosion rates from electrochemical measurements for copper electrodes in LOT test parcel A2 at Äspö and in the retrieved bentonite test package (btp). (The corrosion rates are given for n=1 and corrected for the applied measuring frequency (Rosborg et al. 2004a).)**

| Position         | Installed | Retrieved | Exposure years | Temp °C | Corrosion rate µm/year | Ref |
|------------------|-----------|-----------|----------------|---------|------------------------|-----|
| PR dh 1          | 2001      |           | 9              | 30      | 0.3                    |     |
| PR dh 5          | 2003      | 2011      | 7              | 35      | 0.4                    |     |
| LOT A2           | 1999      | 2006      | 6              | 24      | 0.8                    | a   |
| btp pre-exposed  | 1999/2006 | 2011      | 6+5*           | RT      | 0.7                    |     |
| btp new          | 2006      | 2011      | 5              | RT      | 0.2                    |     |
| btp ER sensors** | 2007      | 2011      | 4              | RT      | 0.4–0.7                | b   |

a – (Rosborg and Pan 2008); b – (Rosborg et al. 2013b).

\* Exposed in LOT test parcel A2 at Äspö for about 6 years and then in the btp for about 5 years. The btp was surrounded by air.

\*\* Data from EIS measurements.

### 5.3 Comparison with gravimetric data

The *estimated* final corrosion rates for the copper electrodes in dh 1 and dh 5 are compared to average corrosion rates for copper coupons and ER sensors exposed to similar environments in Table 5-3. The copper coupons were exposed in LOT test parcels A0 and A2 and weighed before and after exposure (Karnland et al. 2009, 2011). The electric resistance sensors were exposed in the bentonite test package (btp) for verified oxic conditions, see Figure 3-1, and the average corrosion rates were estimated by comparing cross-sections of corroded and protected sensor elements (Rosborg et al. 2013b).

The *estimated* final corrosion rates for the copper electrodes from the Prototype Repository are the smallest, which is of course expected. However, the average corrosion rates for the LOT A2 coupons are not that far apart. Even if the average corrosion rates of the coupons and sensors in Table 5-3 are in reasonable order considering the length of exposure, they also disclose a discrepancy; the LOT A0 coupons have corroded more in less than two years than the LOT A2 coupons in six years (compare the weight changes). It is obvious that local conditions in the near-field environment (and most certainly differences in start of exposure) can radically influence the amount of corrosion. Also the *estimated* average corrosion rates for the ER sensors exposed in the bentonite test package for nominally the same conditions show a considerable spread.

The *estimated* final corrosion rate from the real-time measurements on the copper electrodes in LOT test parcel A2 (and for their prolonged exposure in the bentonite test package) are considerably higher than the average corrosion rate on the LOT A2 coupons (compare values given in Tables 5-2 and 5-3). The electrochemical real-time measurements may provide higher than actual rates, which has earlier been considered (Rosborg et al. 2005). However, the differences in the acquired corrosion rates could just reflect variability in the near-field environment.

**Table 5-3. Comparison with average corrosion rates from exposure of copper coupons in LOT test parcels and from exposure of electric resistance sensors of pure copper in the bentonite test package (btp).**

| Position       | Installed | Retrieved | Length of exposure<br>years | Temp<br>°C | Corrosion rate<br>µm/year | Weight change<br>mg | Ref |
|----------------|-----------|-----------|-----------------------------|------------|---------------------------|---------------------|-----|
| PR dh 1        | 2001      |           | 9                           | 30         | 0.3                       |                     |     |
| PR dh 5        | 2003      | 2011      | 7                           | 35         | 0.4                       |                     |     |
| LOT A2 coupons | 1999      | 2006      | 6                           | 30         | < 0.5                     | 27–46               | a   |
| LOT A0 coupons | 1999      | 2001      | < 2                         | 35         | 3.4                       | 83–86               | b   |
| btp ER sensors | 2007      | 2011      | 4                           | RT         | 1.6–2.9                   |                     | c   |

a – (Karnland et al. 2009); b – (Karnland et al. 2011); c – (Rosborg et al. 2013b).

## 6 Conclusions

Real-time corrosion monitoring by means of electrochemical methods, using SmartCET<sup>®</sup> corrosion monitoring systems, has been applied on cylindrical copper electrodes in two deposition holes (dh) of the Prototype Repository at Äspö. The *recorded* corrosion rates fall below 1.3  $\mu\text{m}/\text{year}$  (using a default value of  $n=2$  in the software and with no correction applied for the used measuring frequency of 0.01 Hz; also disregarding the highly scattered data obtained for the copper electrodes in dh 1 during 2010).

The *recorded* corrosion rate for the electrodes in dh 5 first increased from about 0.2  $\mu\text{m}/\text{year}$  in 2004 up to a maximum of 1.3  $\mu\text{m}/\text{year}$  a year later and then gradually decreased to 0.7  $\mu\text{m}/\text{year}$  in the end of 2010. The drainage of the inner and outer sections in the Prototype Repository was temporary closed in the end of 2004, and it is anticipated that the bentonite pore water before then was dominated by the bicarbonate containing tap water, and from 2005 on dominated by the saline groundwater in the surrounding rock. It seems somewhat unexpected that the corrosion rate for the copper electrodes in dh 1 did not show the same behaviour; however, the *recorded* corrosion rates for these electrodes are lower and the copper electrodes have been exposed longer.

Since the major corrosion product formed is cuprite, it is more relevant to use  $n=1$  in Faraday's law to convert the corrosion current density to a penetration rate. Furthermore, electrochemical impedance spectroscopy on pure copper electrodes in Äspö groundwater open to air has shown that the applied measuring frequency underestimates the polarization resistance with a factor of 4, and thus overestimates the corrosion rate with the same amount. After applying these corrections *better estimates* of the corrosion rates in the end of 2010 fall below 0.4  $\mu\text{m}/\text{year}$ . Assuming that the correction for the measuring frequency is correct this is the highest possible corrosion rate. The actual corrosion rate could be lower due to parallel redox reactions.

The *estimated* corrosion rates on the copper electrodes in the Prototype Repository are lower than the rate estimated for the copper electrodes in LOT test parcel A2, about 0.4 compared to 0.8  $\mu\text{m}/\text{year}$  after six years exposure respectively. Different operating conditions may be the reason for this. The average corrosion rate obtained from weight measurements of copper coupons in LOT test parcel A2 was found to be less than 0.5  $\mu\text{m}/\text{year}$ , indicating that the real-time corrosion monitoring may provide conservative corrosion rates. Otherwise it just reflects variability in the near-field environment.



## Acknowledgements

Christina Lilja and Lars Werme at the SKB head office in Stockholm, and the staff at the Äspö Hard Rock Laboratory are gratefully acknowledged for their contributions. Special thanks to Stefan Grandin Svärth for excellent support during the measurements.

## References

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

- ASTM G96 – 90(2008)**. Standard guide for online monitoring of corrosion in plant equipment (Electrical and electrochemical methods). West Conshohocken, PA: ASTM International.
- ASTM G102 – 89(2010)**. Standard practice for calculation of corrosion rates and related information from electrochemical measurements. West Conshohocken, PA: ASTM International.
- Brossia C S, 2008**. Electrical resistance techniques. In Yang L (ed). *Techniques for corrosion monitoring*. Cambridge: Woodhead Publishing Limited, 277–292.
- Cottis R, 2008**. Electrochemical noise for corrosion monitoring. In Yang L (ed). *Techniques for corrosion monitoring*. Cambridge: Woodhead Publishing Limited, 86–110.
- Cottis R, Turgoose S, 1999**. *Electrochemical impedance and noise*. Houston, TX: NACE International.
- Darowicki K, Majewska J, 1999**. Harmonic analysis of electrochemical and corrosion systems – a review. *Corrosion Reviews* 17, 383–399.
- Johannesson L-E, 2002**. Äspö Hard Rock Laboratory. Manufacturing of bentonite buffer for the prototype repository. SKB IPR-02-19, Svensk Kärnbränslehantering AB.
- Johannesson L-E, Gunnarsson D, Sandén T, Börgesson L, Karlzén R, 2004**. Äspö Hard Rock Laboratory. Prototype repository. Installation of buffer, canisters, backfill, plug and instruments in Section II. SKB IPR-04-13, Svensk Kärnbränslehantering AB.
- Karnland O, Olsson S, Nilsson U, 2006**. Mineralogy and sealing properties of various bentonites and smectite-rich clay materials. SKB TR-06-30, Svensk Kärnbränslehantering AB.
- Karnland O, Olsson S, Dueck A, Birgersson M, Nilsson U, Hernan-Håkansson T, Pedersen K, Nilsson S, Eriksen T E, Rosborg B, 2009**. Long term test of buffer material at the Äspö Hard Rock Laboratory, LOT project. Final report on the A2 test parcel. SKB TR-09-29, Svensk Kärnbränslehantering AB.
- Karnland O, Olsson S, Sandén T, Fälth B, Jansson M, Eriksen T E, Svärdström K, Rosborg B, Muurinen A, 2011**. Long term test of buffer material at the Äspö HRL, LOT project. Final report on the A0 test parcel. SKB TR-09-31, Svensk Kärnbränslehantering AB.
- King F, Ahonen L, Taxén T, Vuorinen U, Werme L, 2001**. Copper corrosion under expected conditions in a deep geologic repository. SKB TR-01-23, Svensk Kärnbränslehantering AB.
- King F, Lilja C, Pedersen K, Pitkänen P, Vähänen M, 2010**. An update of the state-of-the-art report on the corrosion of copper under expected conditions in a deep geological repository. SKB TR-10-67, Svensk Kärnbränslehantering AB.
- Laaksoharju M, Gurban I, Skårman C, 1998**. Summary of hydrochemical conditions at Aberg, Beberg and Ceberg. SKB TR 98-03, Svensk Kärnbränslehantering AB.
- Rosborg B, Pan J, 2008**. An electrochemical impedance spectroscopy study of copper in a bentonite/saline groundwater environment. *Electrochimica Acta* 53, 7556–7564.
- Rosborg B, Werme L, 2008**. The Swedish nuclear waste program and the long-term corrosion behaviour of copper. *Journal of Nuclear Materials* 379, 142–153.
- Rosborg B, Eden D, Karnland O, Pan J, Werme L, 2004a**. The corrosion rate of copper in a test parcel at the Äspö Hard Rock Laboratory. In Oversby V M, Werme L O (eds). *Scientific basis for nuclear waste management XXVII: symposium held in Kalmar, Sweden, 15–19 June 2003*. Warrendale, PA: Materials Research Society. (Materials Research Society Symposium Proceedings 807), 489–494.

- Rosborg B, Eden D, Karnland O, Pan J, Werme L, 2004b.** Real-time monitoring of copper corrosion at the Äspö HRL. In Féron D, Macdonald D D (eds). Prediction of long term corrosion behaviour in nuclear waste systems: proceedings of the 2nd International Workshop Organized by the Working Party on Nuclear Corrosion (WP4) of the European Federation of Corrosion (EFC), Nice, September 2004 (EUROCORR'2004). Châtenay-Malabry, France: Andra, 11–23.
- Rosborg B, Pan J, Leygraf C, 2005.** Tafel slopes used in monitoring of copper corrosion in a bentonite/groundwater environment. *Corrosion Science* 47, 3267–3279.
- Rosborg B, Kosec T, Kranjc A, Pan J, Legat A, 2011a.** Electrochemical impedance spectroscopy of pure copper exposed in bentonite under oxic conditions. *Electrochimica Acta* 56, 7862–7870.
- Rosborg B, Kranjc A, Kuhar V, Legat A, 2011b.** Corrosion rate of pure copper in an oxic bentonite/saline groundwater environment. *Corrosion Engineering, Science and Technology* 46, 148–152.
- Rosborg B, 2013a.** Post-test examination of a copper electrode from deposition hole 5 in the Prototype repository. SKB R-13-14, Svensk Kärnbränslehantering AB.
- Rosborg B, Kosec T, Kranjc A, Kuhar V, Legat A, 2013b.** The corrosion rate of copper in a bentonite test package measured with electrical resistance sensors. SKB R-13-15, Svensk Kärnbränslehantering AB.
- Scully J R, 2000.** Polarization resistance method for determination of instantaneous corrosion rates. *Corrosion* 56, 199–217.
- Scully J R, 2003.** The polarization resistance method for determination of instantaneous corrosion rates. In Kelly R G, Scully J R, Shoesmith D W, Buchheit R G (eds). *Electrochemical techniques in corrosion science and engineering*. New York: Marcel Dekker, 125–150.
- Stern M, Geary A L, 1957.** Electrochemical polarization: I. A theoretical analysis of the shape of polarization curves. *Journal of Electrochemical Society* 104, 56–63.
- Werme L, 1998.** Design premises for canister for spent nuclear fuel. SKB TR-98-08, Svensk Kärnbränslehantering AB.

### Acquired data from dh 1 during 2010

Position of electrodes: In the second upper block (C3) in deposition hole 1 (DA3587G01); at 269, 270 and 271°. Size of each electrode:  $\text{Ø}60 \times 100$  mm; nominal surface area  $232 \text{ cm}^2$ . Two cables from each electrode with black, yellow-green, and red insulation ending in the G-tunnel (HG0026A02). Heat to the copper canister from 2001-09-17; the electrodes installed a few days earlier. The table contains data for every 6 h during the measuring period 2010-10-28–2010-11-22.

### SmartCET® unit, probe and electrode connection:

KTH lab unit; Probe 2; Black to AB – YG to CD – Blue to EF

### Preset values:

Electrode area =  $232 \text{ cm}^2$ .

B (Stern-Geary coefficient) =  $10.3 \text{ mV}$ .

$n = 2$ .

Density =  $8.94 \text{ g/cm}^3$ .

Atomic weight =  $63.54$ .

Resistance =  $50 \text{ ohm}$ .

### Explanation of table:

HDA **Corr rate**=Recorded corrosion rate from harmonic distortion analysis.

PR **Corr rate**=Recorded corrosion rate from polarisation resistance measurements using the actual B-value.

B=Stern-Geary coefficient.

$\beta_a$ =Exponential anodic Tafel coefficient.

$\beta_c$ =Exponential cathodic Tafel coefficient.

| Date/Time        | HDA<br>Corr rate<br>$\mu\text{m}/\text{year}$ | PR<br>Corr rate<br>$\mu\text{m}/\text{year}$ | B<br>mV | $\beta_a$<br>mV | $\beta_c$<br>mV |
|------------------|---|--|---------|-----------------|-----------------|
| 2010-10-28 19:16 | 0.75  | 0.75   | 9.44    | 16.99           | 21.25           |
| 2010-10-29 00:02 | 0.78  | 0.78   | 10.17   | 17.12           | 25.05           |
| 2010-10-29 06:01 | 1.08  | 1.08   | 14.10   | 22.67           | 37.30           |
| 2010-10-29 12:00 | 0.73  | 0.73   | 9.04    | 15.52           | 21.66           |
| 2010-10-29 18:06 | 0.84  | 0.84   | 10.67   | 17.23           | 28.02           |
| 2010-10-30 00:04 | 0.67  | 0.67   | 8.03    | 13.54           | 19.72           |
| 2010-10-30 06:02 | 0.67  | 0.67   | 7.91    | 13.40           | 19.29           |
| 2010-10-30 12:01 | 0.68  | 0.68   | 8.14    | 13.67           | 20.14           |
| 2010-10-30 18:06 | 0.65  | 0.65   | 7.82    | 13.21           | 19.19           |
| 2010-10-31 00:05 | 0.71  | 0.71   | 8.59    | 14.34           | 21.43           |
| 2010-10-31 06:01 | 0.71  | 0.71   | 8.66    | 14.40           | 21.71           |
| 2010-10-31 12:06 | 0.66  | 0.66   | 7.85    | 13.28           | 19.19           |
| 2010-10-31 18:05 | 0.64  | 0.64   | 7.49    | 12.89           | 17.87           |
| 2010-11-01 00:03 | 0.70  | 0.70   | 8.67    | 14.40           | 21.79           |
| 2010-11-01 06:01 | 0.86  | 0.86   | 10.89   | 17.50           | 28.85           |
| 2010-11-01 12:00 | 0.80  | 0.80   | 9.95    | 16.47           | 25.12           |
| 2010-11-01 18:06 | 0.66  | 0.66   | 7.90    | 13.33           | 19.41           |
| 2010-11-02 00:04 | 0.74  | 0.74   | 9.27    | 15.35           | 23.37           |
| 2010-11-02 06:02 | 1.13  | 1.13   | 14.86   | 23.08           | 41.71           |
| 2010-11-02 12:01 | 0.94  | 0.94   | 12.07   | 19.47           | 31.75           |
| 2010-11-02 18:06 | 0.87  | 0.87   | 11.26   | 18.11           | 29.78           |
| 2010-11-03 00:05 | 0.67  | 0.67   | 8.39    | 14.11           | 20.70           |
| 2010-11-03 06:03 | 0.66  | 0.66   | 7.93    | 13.34           | 19.54           |
| 2010-11-03 12:02 | 0.59  | 0.59   | 6.64    | 11.60           | 15.52           |
| 2010-11-03 18:01 | 0.63  | 0.63   | 7.70    | 13.13           | 18.62           |
| 2010-11-04 00:07 | 0.96  | 0.96   | 12.45   | 19.76           | 33.63           |
| 2010-11-04 06:05 | 0.93  | 0.93   | 12.62   | 21.37           | 30.81           |
| 2010-11-04 12:04 | 0.67  | 0.66   | 9.28    | 16.75           | 20.82           |
| 2010-11-04 18:03 | 0.47  | 0.47   | 6.65    | 13.08           | 13.54           |
| 2010-11-05 00:01 | 0.47  | 0.47   | 6.64    | 12.87           | 13.71           |
| 2010-11-05 06:00 | 0.50  | 0.50   | 7.07    | 13.53           | 14.82           |
| 2010-11-05 12:06 | 0.39  | 0.39   | 5.38    | 10.61           | 10.90           |
| 2010-11-05 18:05 | 0.46  | 0.46   | 5.82    | 11.27           | 12.03           |
| 2010-11-06 00:03 | 0.48  | 0.48   | 5.95    | 11.47           | 12.38           |
| 2010-11-06 06:02 | 0.49  | 0.49   | 5.95    | 11.32           | 12.53           |
| 2010-11-06 12:01 | 0.50  | 0.50   | 6.10    | 11.76           | 12.67           |
| 2010-11-06 18:00 | 0.51  | 0.51   | 6.09    | 11.59           | 12.83           |
| 2010-11-07 00:05 | 0.54  | 0.54   | 6.39    | 12.07           | 13.56           |
| 2010-11-07 06:04 | 0.53  | 0.53   | 6.13    | 11.57           | 13.04           |
| 2010-11-07 12:03 | 0.54  | 0.54   | 6.29    | 11.89           | 13.36           |
| 2010-11-07 18:02 | 0.55  | 0.55   | 6.40    | 12.08           | 13.61           |
| 2010-11-08 00:00 | 0.53  | 0.53   | 6.19    | 11.64           | 13.20           |
| 2010-11-08 06:06 | 0.55  | 0.55   | 6.30    | 11.91           | 13.39           |
| 2010-11-08 12:05 | 0.53  | 0.53   | 6.24    | 11.80           | 13.24           |
| 2010-11-08 18:04 | 0.53  | 0.53   | 6.31    | 11.92           | 13.40           |
| 2010-11-09 00:02 | 0.49  | 0.49   | 5.94    | 11.40           | 12.41           |
| 2010-11-09 06:01 | 0.47  | 0.47   | 5.89    | 11.41           | 12.15           |
| 2010-11-09 12:00 | 0.44  | 0.44   | 5.73    | 11.25           | 11.70           |
| 2010-11-09 18:06 | 0.85  | 0.85   | 11.54   | 19.79           | 27.67           |
| 2010-11-10 00:04 | 0.59  | 0.59   | 8.24    | 15.71           | 17.31           |
| 2010-11-10 06:03 | 0.40  | 0.40   | 5.48    | 10.83           | 11.10           |
| 2010-11-10 12:02 | 0.45  | 0.45   | 5.82    | 11.26           | 12.06           |
| 2010-11-10 18:00 | 0.45  | 0.45   | 5.77    | 11.30           | 11.79           |
| 2010-11-11 00:06 | 0.42  | 0.42   | 5.58    | 11.03           | 11.31           |
| 2010-11-11 06:05 | 0.44  | 0.44   | 5.75    | 11.27           | 11.72           |

| Date/Time        | HDA<br>Corr rate<br>$\mu\text{m}/\text{year}$ | PR<br>Corr rate<br>$\mu\text{m}/\text{year}$ | B<br>mV | $\beta_a$<br>mV | $\beta_c$<br>mV |
|------------------|---|--|---------|-----------------|-----------------|
| 2010-11-11 12:04 | 0.45  | 0.45   | 5.71    | 11.04           | 11.84           |
| 2010-11-11 18:02 | 0.44  | 0.44   | 5.71    | 11.26           | 11.59           |
| 2010-11-12 00:01 | 0.42  | 0.42   | 5.85    | 11.61           | 11.79           |
| 2010-11-12 06:00 | 0.52  | 0.52   | 7.41    | 14.09           | 15.62           |
| 2010-11-12 12:06 | 0.58  | 0.58   | 8.11    | 15.05           | 17.58           |
| 2010-11-12 18:04 | 1.02  | 1.02   | 13.39   | 21.17           | 36.42           |
| 2010-11-13 00:03 | 0.89  | 0.89   | 11.21   | 18.35           | 28.81           |
| 2010-11-13 06:02 | 0.88  | 0.88   | 11.32   | 18.30           | 29.68           |
| 2010-11-13 12:01 | 0.88  | 0.88   | 11.38   | 18.31           | 30.07           |
| 2010-11-13 18:06 | 1.06  | 1.06   | 13.95   | 22.15           | 37.70           |
| 2010-11-14 00:05 | 0.92  | 0.92   | 12.02   | 19.94           | 30.25           |
| 2010-11-14 06:04 | 0.85  | 0.85   | 11.51   | 19.56           | 27.98           |
| 2010-11-14 12:03 | 0.99  | 0.99   | 13.46   | 22.55           | 33.38           |
| 2010-11-14 18:01 | 1.00  | 1.00   | 13.12   | 21.62           | 33.39           |
| 2010-11-15 00:00 | 0.91  | 0.91   | 12.04   | 19.41           | 31.69           |
| 2010-11-15 06:06 | 0.74  | 0.74   | 9.61    | 15.90           | 24.26           |
| 2010-11-15 12:04 | 0.66  | 0.66   | 7.88    | 13.33           | 19.29           |
| 2010-11-15 18:03 | 0.78  | 0.78   | 9.89    | 16.48           | 24.74           |
| 2010-11-16 00:02 | 0.94  | 0.94   | 12.57   | 20.25           | 33.16           |
| 2010-11-16 06:01 | 0.54  | 0.54   | 7.62    | 14.56           | 15.97           |
| 2010-11-16 12:06 | 0.48  | 0.48   | 6.68    | 12.99           | 13.75           |
| 2010-11-16 18:05 | 0.41  | 0.41   | 5.69    | 11.19           | 11.56           |
| 2010-11-17 00:04 | 0.41  | 0.41   | 5.48    | 10.95           | 10.96           |
| 2010-11-17 06:03 | 0.44  | 0.44   | 5.76    | 11.22           | 11.85           |
| 2010-11-17 12:01 | 0.44  | 0.44   | 6.16    | 12.01           | 12.66           |
| 2010-11-17 18:00 | 0.42  | 0.42   | 5.84    | 11.57           | 11.79           |
| 2010-11-18 00:06 | 0.40  | 0.40   | 5.46    | 10.93           | 10.93           |
| 2010-11-18 06:05 | 0.45  | 0.45   | 6.24    | 12.34           | 12.63           |
| 2010-11-18 12:03 | 0.39  | 0.39   | 5.26    | 10.39           | 10.64           |
| 2010-11-18 18:02 | 0.43  | 0.43   | 5.66    | 11.21           | 11.43           |
| 2010-11-19 00:01 | 0.45  | 0.45   | 5.80    | 11.31           | 11.91           |
| 2010-11-19 06:00 | 0.42  | 0.42   | 5.53    | 10.76           | 11.38           |
| 2010-11-19 12:06 | 0.40  | 0.40   | 5.34    | 10.55           | 10.80           |
| 2010-11-19 18:05 | 0.40  | 0.40   | 5.60    | 11.05           | 11.35           |
| 2010-11-20 00:03 | 0.81  | 0.81   | 11.27   | 20.06           | 25.73           |
| 2010-11-20 06:02 | 0.79  | 0.79   | 10.14   | 16.61           | 26.03           |
| 2010-11-20 12:01 | 0.75  | 0.75   | 9.25    | 15.32           | 23.35           |
| 2010-11-20 18:00 | 0.73  | 0.73   | 9.00    | 15.15           | 22.19           |
| 2010-11-21 00:05 | 0.74  | 0.74   | 9.19    | 15.19           | 23.26           |
| 2010-11-21 06:04 | 0.68  | 0.68   | 8.39    | 14.12           | 20.67           |
| 2010-11-21 12:03 | 0.68  | 0.68   | 8.42    | 14.09           | 20.91           |
| 2010-11-21 18:02 | 0.79  | 0.79   | 9.78    | 16.20           | 24.67           |
| 2010-11-22 00:00 | 0.77  | 0.77   | 9.71    | 16.03           | 24.59           |
| 2010-11-22 06:06 | 0.73  | 0.73   | 9.23    | 15.32           | 23.19           |
| 2010-11-22 12:05 | 0.72  | 0.72   | 8.93    | 14.82           | 22.46           |
| 2010-11-22 15:26 | 0.94  | 0.94   | 12.17   | 19.54           | 32.27           |

### Acquired data from dh 5 during 2010

Position of electrodes: In the upper block (C4) in deposition hole 5 (DA3551G01); at 269, 270 and 271°. Size of each electrode:  $\text{Ø}60 \times 100$  mm; nominal surface area 232 cm<sup>2</sup>. Two cables from each electrode with black, yellow-green, and red insulation ending in the G-tunnel (HG0023A02). The table contains data for every 6 h during the measuring period 2010-10-29–2010-11-22.

### SmartCET<sup>®</sup> unit, probe and electrode connection:

KTH lab unit; Probe 1; Black to AB – YG to CD – Red to EF

### Preset values:

Electrode area = 232 cm<sup>2</sup>.

B (Stern-Geary coefficient) = 10.3 mV.

n = 2.

Density = 8.94 g/cm<sup>3</sup>.

Atomic weight = 63.54.

Resistance = 50 ohm.

### Explanation of table:

HDA **Corr rate**=Recorded corrosion rate from harmonic distortion analysis.

PR **Corr rate**=Recorded corrosion rate from polarisation resistance measurements using the actual B-value.

B=Stern-Geary coefficient.

$\beta_a$ =Exponential anodic Tafel coefficient.

$\beta_c$ =Exponential cathodic Tafel coefficient.

| Date/Time        | HDA<br>Corr rate<br>$\mu\text{m}/\text{year}$ | PR<br>Corr rate<br>$\mu\text{m}/\text{year}$ | B<br>mV | $\beta_a$<br>mV | $\beta_c$<br>mV |
|------------------|---|--|---------|-----------------|-----------------|
| 2010-10-29 18:06 | 0.72  | 0.72   | 6.15    | 11.52           | 13.21           |
| 2010-10-30 00:04 | 0.73  | 0.73   | 6.25    | 11.66           | 13.47           |
| 2010-10-30 06:02 | 0.71  | 0.71   | 6.14    | 11.52           | 13.14           |
| 2010-10-30 12:01 | 0.70  | 0.70   | 6.10    | 11.46           | 13.04           |
| 2010-10-30 18:06 | 0.69  | 0.69   | 6.04    | 11.37           | 12.88           |
| 2010-10-31 00:05 | 0.69  | 0.69   | 6.06    | 11.44           | 12.90           |
| 2010-10-31 06:01 | 0.69  | 0.69   | 6.08    | 11.46           | 12.93           |
| 2010-10-31 12:06 | 0.69  | 0.69   | 6.07    | 11.45           | 12.92           |
| 2010-10-31 18:05 | 0.73  | 0.73   | 6.25    | 11.68           | 13.43           |
| 2010-11-01 00:03 | 0.76  | 0.76   | 6.36    | 11.84           | 13.75           |
| 2010-11-01 06:01 | 0.78  | 0.78   | 6.50    | 12.07           | 14.08           |
| 2010-11-01 12:00 | 0.82  | 0.82   | 6.76    | 12.49           | 14.75           |
| 2010-11-01 18:06 | 0.71  | 0.71   | 6.11    | 11.54           | 13.00           |
| 2010-11-02 00:04 | 0.70  | 0.70   | 6.11    | 11.53           | 12.98           |
| 2010-11-02 06:02 | 0.70  | 0.70   | 6.12    | 11.56           | 13.02           |
| 2010-11-02 12:01 | 0.71  | 0.71   | 6.13    | 11.56           | 13.06           |
| 2010-11-02 18:06 | 0.70  | 0.70   | 6.12    | 11.54           | 13.04           |
| 2010-11-03 00:05 | 0.70  | 0.70   | 6.11    | 11.54           | 13.01           |
| 2010-11-03 06:03 | 0.70  | 0.70   | 6.13    | 11.56           | 13.04           |
| 2010-11-03 12:02 | 0.70  | 0.70   | 6.14    | 11.58           | 13.07           |
| 2010-11-03 18:01 | 0.72  | 0.72   | 6.18    | 11.61           | 13.20           |
| 2010-11-04 00:07 | 0.70  | 0.70   | 6.10    | 11.53           | 12.95           |
| 2010-11-04 06:05 | 0.70  | 0.70   | 6.10    | 11.55           | 12.95           |
| 2010-11-04 12:04 | 0.70  | 0.70   | 6.10    | 11.54           | 12.94           |
| 2010-11-04 18:03 | 0.69  | 0.69   | 6.07    | 11.49           | 12.87           |
| 2010-11-05 00:01 | 0.69  | 0.69   | 6.08    | 11.52           | 12.87           |
| 2010-11-05 06:00 | 0.69  | 0.69   | 6.08    | 11.52           | 12.89           |
| 2010-11-05 12:06 | 0.69  | 0.69   | 6.06    | 11.49           | 12.82           |
| 2010-11-05 18:05 | 0.68  | 0.68   | 6.04    | 11.46           | 12.78           |
| 2010-11-06 00:03 | 0.68  | 0.68   | 6.04    | 11.49           | 12.76           |
| 2010-11-06 06:02 | 0.68  | 0.69   | 6.05    | 11.50           | 12.78           |
| 2010-11-06 12:01 | 0.68  | 0.68   | 6.04    | 11.47           | 12.77           |
| 2010-11-06 18:00 | 0.68  | 0.68   | 6.03    | 11.46           | 12.73           |
| 2010-11-07 00:05 | 0.68  | 0.68   | 6.04    | 11.48           | 12.74           |
| 2010-11-07 06:04 | 0.69  | 0.69   | 6.06    | 11.51           | 12.79           |
| 2010-11-07 12:03 | 0.69  | 0.69   | 6.05    | 11.50           | 12.79           |
| 2010-11-07 18:02 | 0.68  | 0.68   | 6.04    | 11.47           | 12.75           |
| 2010-11-08 00:00 | 0.69  | 0.69   | 6.06    | 11.51           | 12.79           |
| 2010-11-08 06:06 | 0.69  | 0.69   | 6.06    | 11.52           | 12.80           |
| 2010-11-08 12:05 | 0.69  | 0.69   | 6.06    | 11.51           | 12.80           |
| 2010-11-08 18:04 | 0.69  | 0.68   | 6.06    | 11.50           | 12.78           |
| 2010-11-09 00:02 | 0.69  | 0.69   | 6.09    | 11.56           | 12.86           |
| 2010-11-09 06:01 | 0.69  | 0.69   | 6.08    | 11.53           | 12.85           |
| 2010-11-09 12:00 | 0.69  | 0.69   | 6.07    | 11.49           | 12.84           |
| 2010-11-09 18:06 | 0.69  | 0.69   | 6.07    | 11.51           | 12.86           |
| 2010-11-10 00:04 | 0.69  | 0.69   | 6.08    | 11.55           | 12.85           |
| 2010-11-10 06:03 | 0.69  | 0.69   | 6.08    | 11.55           | 12.85           |
| 2010-11-10 12:02 | 0.69  | 0.69   | 6.07    | 11.51           | 12.83           |
| 2010-11-10 18:00 | 0.68  | 0.68   | 6.06    | 11.51           | 12.79           |
| 2010-11-11 00:06 | 0.69  | 0.69   | 6.09    | 11.56           | 12.85           |
| 2010-11-11 06:05 | 0.69  | 0.69   | 6.07    | 11.54           | 12.82           |
| 2010-11-11 12:04 | 0.69  | 0.69   | 6.08    | 11.54           | 12.84           |
| 2010-11-11 18:02 | 0.68  | 0.68   | 6.05    | 11.52           | 12.75           |
| 2010-11-12 00:01 | 0.68  | 0.68   | 6.07    | 11.55           | 12.81           |
| 2010-11-12 06:00 | 0.68  | 0.68   | 6.08    | 11.56           | 12.83           |



| Date/Time        | HDA<br>Corr rate<br>$\mu\text{m}/\text{year}$ | PR<br>Corr rate<br>$\mu\text{m}/\text{year}$ | B<br>mV | $\beta_a$<br>mV | $\beta_c$<br>mV |
|------------------|---|--|---------|-----------------|-----------------|
| 2010-11-12 12:06 | 0.69  | 0.69   | 6.08    | 11.54           | 12.83           |
| 2010-11-12 18:04 | 0.69  | 0.69   | 6.07    | 11.54           | 12.81           |
| 2010-11-13 00:03 | 0.69  | 0.69   | 6.09    | 11.58           | 12.86           |
| 2010-11-13 06:02 | 0.69  | 0.69   | 6.10    | 11.59           | 12.87           |
| 2010-11-13 12:01 | 0.69  | 0.69   | 6.09    | 11.57           | 12.85           |
| 2010-11-13 18:06 | 0.69  | 0.68   | 6.07    | 11.54           | 12.80           |
| 2010-11-14 00:05 | 0.69  | 0.69   | 6.09    | 11.59           | 12.86           |
| 2010-11-14 06:04 | 0.69  | 0.69   | 6.10    | 11.60           | 12.87           |
| 2010-11-14 12:03 | 0.69  | 0.69   | 6.08    | 11.56           | 12.83           |
| 2010-11-14 18:01 | 0.69  | 0.69   | 6.10    | 11.60           | 12.87           |
| 2010-11-15 00:00 | 0.69  | 0.69   | 6.11    | 11.60           | 12.89           |
| 2010-11-15 06:06 | 0.69  | 0.69   | 6.10    | 11.60           | 12.88           |
| 2010-11-15 12:04 | 0.69  | 0.69   | 6.09    | 11.56           | 12.86           |
| 2010-11-15 18:03 | 0.68  | 0.68   | 6.08    | 11.57           | 12.79           |
| 2010-11-16 00:02 | 0.68  | 0.68   | 6.06    | 11.53           | 12.78           |
| 2010-11-16 06:01 | 0.68  | 0.68   | 6.06    | 11.51           | 12.78           |
| 2010-11-16 12:06 | 0.68  | 0.68   | 6.04    | 11.48           | 12.76           |
| 2010-11-16 18:05 | 0.68  | 0.68   | 6.04    | 11.49           | 12.73           |
| 2010-11-17 00:04 | 0.68  | 0.68   | 6.06    | 11.53           | 12.78           |
| 2010-11-17 06:03 | 0.68  | 0.68   | 6.06    | 11.52           | 12.79           |
| 2010-11-17 12:01 | 0.68  | 0.68   | 6.05    | 11.50           | 12.75           |
| 2010-11-17 18:00 | 0.68  | 0.68   | 6.06    | 11.53           | 12.77           |
| 2010-11-18 00:06 | 0.68  | 0.68   | 6.06    | 11.53           | 12.76           |
| 2010-11-18 06:05 | 0.68  | 0.68   | 6.07    | 11.55           | 12.79           |
| 2010-11-18 12:03 | 0.68  | 0.68   | 6.07    | 11.54           | 12.78           |
| 2010-11-18 18:02 | 0.69  | 0.69   | 6.09    | 11.60           | 12.84           |
| 2010-11-19 00:01 | 0.68  | 0.68   | 6.09    | 11.58           | 12.82           |
| 2010-11-19 06:00 | 0.68  | 0.68   | 6.07    | 11.56           | 12.78           |
| 2010-11-19 12:06 | 0.68  | 0.68   | 6.07    | 11.56           | 12.79           |
| 2010-11-19 18:05 | 0.68  | 0.68   | 6.07    | 11.54           | 12.79           |
| 2010-11-20 00:03 | 0.68  | 0.68   | 6.06    | 11.53           | 12.76           |
| 2010-11-20 06:02 | 0.68  | 0.68   | 6.05    | 11.53           | 12.75           |
| 2010-11-20 12:01 | 0.68  | 0.68   | 6.07    | 11.55           | 12.77           |
| 2010-11-20 18:00 | 0.68  | 0.68   | 6.08    | 11.57           | 12.81           |
| 2010-11-21 00:05 | 0.68  | 0.68   | 6.07    | 11.55           | 12.80           |
| 2010-11-21 06:04 | 0.68  | 0.68   | 6.06    | 11.54           | 12.77           |
| 2010-11-21 12:03 | 0.68  | 0.68   | 6.07    | 11.57           | 12.78           |
| 2010-11-21 18:02 | 0.68  | 0.68   | 6.08    | 11.58           | 12.81           |
| 2010-11-22 00:00 | 0.68  | 0.68   | 6.06    | 11.54           | 12.77           |
| 2010-11-22 06:06 | 0.68  | 0.68   | 6.05    | 11.52           | 12.75           |