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Post-test examination of a copper electrode from deposition hole 5 in the Prototype Repository

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April 2013

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Summary

Three copper electrodes have been exposed for eight years in the outer section of the Prototype Repository at Äspö. The electrodes were installed in the upper bentonite block of deposition hole 5 in May 2003. Most of the time the temperature of the electrodes has been somewhat below 35°C. The electrodes were retrieved for post-test examination in September 2011. This report presents results from electrochemical measurements and the post-test examination of one of the electrodes.

The corrosion potential of the examined copper electrode was –40 mV SHE (2011-02-04) when part of the concrete plug to the outer section of the repository had been removed and made measurements possible. When the back-fill in the deposition tunnel had been removed it was 25 mV SHE (2011-09-12). Finally, before letting loose the copper electrode from the retrieved bentonite block, the corrosion potential was found to be 165 mV SHE (2011-11-15) being a sign of air ingress to the electrode/bentonite interface.

It was immediately obvious from the appearance of the copper electrode, when part of the surrounding bentonite had been removed, that both Cu(I) and Cu(II) corrosion products existed on the electrode surface. X-ray diffraction measurements also verified the presence of cuprite, Cu_2O , and malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$, on the electrode; however, paratacamite, $\text{Cu}_2(\text{OH})_3\text{Cl}$, was not found. The performed Fourier transform infrared and Raman spectroscopy confirmed these observations. The corrosion product film, of which cuprite is the main part, was quite uneven and porous. No unmistakable signs of pitting have been found.

The appearance of the copper electrode reminded of the coupons from the retrieved LOT test parcels, but was different from the appearance of the surface on the full-size canisters. For the latter blue-green Cu(II) corrosion products have not or only rarely been observed from visual examination immediately after removing the surrounding bentonite. Differences that can have a marked influence on the corrosion behaviour between the exposed small samples and the big components exist. The most convincing is that lubricants were used in manufacturing of the full-size bentonite blocks and rings (so available machines could handle the required pressure); lubricants have neither been used for the copper electrodes in the Prototype Repository, nor for the copper coupons in the LOT test parcels.

Based upon the performed corrosion potential measurements and the findings from the post-test examination the following scenario of exposure is envisaged: When installed the copper electrode had merely a very thin cuprite film on the surface from exposure in air. After some length of exposure a corrosion potential was reached that allowed formation of Cu(II) corrosion products. Since the chloride activity in the pore water from start of exposure was low (the bentonite had been conditioned with tap water), malachite rather than paratacamite was formed. Later on the corrosion potential has decreased, influenced by changes in the near-field environment and filming of the surface, and obtained a corrosion potential of –40 mV SHE at the time when part of the concrete plug to the outer section had been removed, which indicates a mildly oxidizing environment. Thus, it is anticipated that the copper electrode has been exposed to oxic conditions all through the exposure period.

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1 Background

This report starts with a brief account of the Prototype Repository in the Äspö Hard Rock Laboratory (HRL), the exposed copper electrodes and the near-field environment, and the retrieval of the copper electrodes from deposition hole 5 (dh 5) in the outer section of the repository after eight years exposure.

1.1 The Prototype Repository

Up to 2011 the Prototype Repository consisted 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 that contained two canisters. The inner section was sealed during 2001 and the outer during 2003. During 2011 the canisters in the outer section were retrieved and so were the copper electrodes in dh 5.

Electrical heaters generated 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 1-1. The original dimensions of the bentonite blocks and rings were about $\text{Ø}1.65 \times 0.50$ m and $\text{Ø}_{\text{outer}} 1.65 \times \text{Ø}_{\text{inner}} 1.07 \times 0.50$ m respectively.

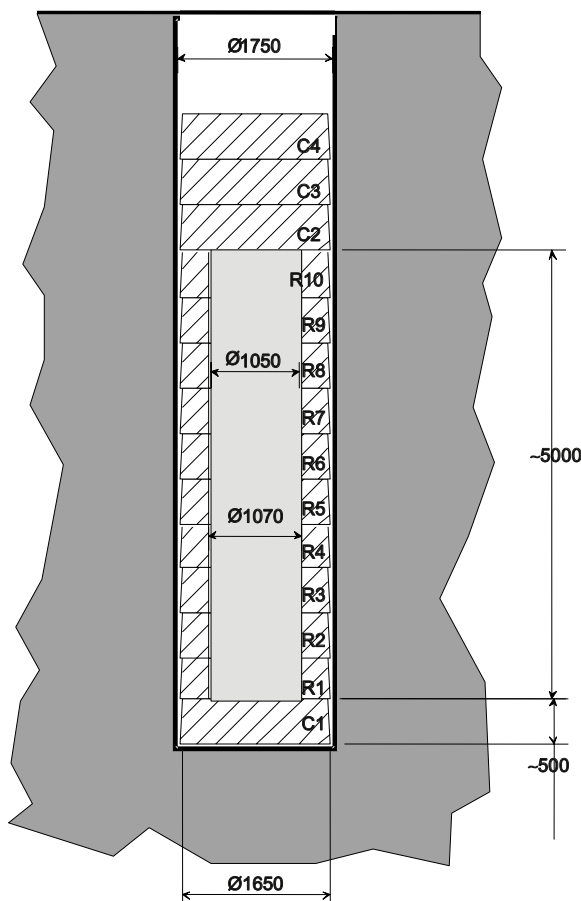


Figure 1-1. A canister in its deposition hole surrounded by bentonite rings and blocks. (The copper electrodes were positioned in the upper bentonite block C4.)

1.2 The copper electrodes

Three nominally identical cylindrical copper electrodes were installed in the upper bentonite block C4 of dh 5 in the outer section of the Prototype Repository, thus above the canister, a few days before the heat was turned on to the canister in May 2003. The electrodes were manufactured from pure copper of canister quality and primarily installed to permit real-time corrosion monitoring.

Real-time SmartCET^{®1} corrosion monitoring has been performed in periods starting in January 2004 (Rosborg 2013). The opportunity to measure the corrosion potential of the electrodes was, however, first realized on 2011-02-04 when part of the concrete plug to the outer section had been removed.

Here follows additional information about the copper electrodes:

- Size of each electrode: Ø60×100 mm; nominal surface area 232 cm².
- Installation in dh 5 (DA3551G01): Ø60 mm holes were first drilled in bentonite block C4 to a depth of 250 mm, the electrodes were placed in the holes after which the holes were refilled with bentonite powder.
- Position of electrodes in the bentonite block (C4): at 269, 270 and 271°.
- Two cables were connected to each electrode with black, yellow-green, and red insulation; the cables ended in the G-tunnel (hole HG0026A02); the electrodes were denoted “Black”, “YG” (yellow-green) and “Red” respectively in the documentation in accordance with Table 1-1.
- Heat to the copper canister in dh 5 from 2003-05-08; the electrodes installed a few days earlier.

1.3 The environment

The bentonite block was manufactured of Wyoming bentonite sold under the commercial name MX-80 and which is dominated by natural sodium montmorillonite. The bentonite powder was of the same quality. The bentonite had been conditioned with tap water² to a water ratio of 17.5% before manufacturing of the bentonite block (Johannesson 2002).

The chemical environment in the electrode/bentonite interface is determined by the composition of the bentonite pore water. From start of exposure it was dominated by tap water. Later on the pore water will be determined by the interaction between the bentonite and the saline groundwater in the surrounding rock. A typical groundwater composition from the Äspö HRL is shown in Table 1-2.

Table 1-1. The copper electrodes in the upper bentonite block of deposition hole 5 in the Prototype Repository with their cable connections.

Name	Position	Cable 1	Cable 2
Black	271°	Black 1	Black 2
YG	270°	YG 1	YG 2
Red	269°	Red 1	Red 2

¹ The equipment is today obtained from Honeywell Process Solutions, 2,500 W. Union Hills Dr., Phoenix, AZ 85027, USA.

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

Table 1-2. Äspö groundwater.

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

Entrapped oxygen will be consumed through reactions with minerals in the bentonite, through copper corrosion, and also through microbial activity (King et al. 2010). The corrosion potential, or redox potential, during the exposure has not been measured.

In November 2004 the drainage to the inner and outer sections of the Prototype Repository was closed, which caused apparent changes in the surrounding bentonite and backfill (Goudarzi and Johannesson 2005). 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. Between 2004 and 2005 the recorded corrosion rate increased considerably (Rosborg 2013).

Most of the time the temperature of the electrodes has been somewhat below 35°C. Further information about the environmental conditions in bentonite block C4 is found in Appendix A.

1.4 Retrieval of electrodes

Stitch drilling to let loose a smaller bentonite block containing the copper electrodes from bentonite block C4 was initiated on 2011-09-19. A series of holes was drilled around the place for the three electrodes, the bentonite block was broken loose from block C4 by bending, and the released bentonite block with the electrodes was lifted up the following day, see Figure 1-2.

Before then the following steps had been taken:

- Work to remove the concrete plug to the external section of the Prototype Repository started on 2010-11-22.
- Heat to the canister in dh 5 was turned off on 2011-02-01.
- The corrosion potential of the copper electrodes was first measured on 2011-02-04 when part of the concrete plug to the outer section had been removed, and it was thus possible to drill a hole through the remaining wall of prefabricated concrete beams and place a reference electrode in contact with the back-fill.
- The concrete plug had been entirely removed on 2011-02-17.
- Most of the backfill in the deposition tunnel up to and above dh 5 had been removed on 2011-08-26 (and backfill on the tunnel floor in the outer section had been removed on 2011-09-06).
- The corrosion potential of the copper electrodes was again measured on 2011-09-09 and 2011-09-12 when reference electrodes could be placed in the remaining backfill just above the copper electrodes; about 85 cm backfill still remained on top of bentonite block C4.

Thus, the copper electrodes that were retrieved on 2011-09-20 have been exposed more than eight years in the Prototype Repository. After the uplift the small bentonite block with the electrodes was immediately packed in triplicate evacuated tri-laminate³ bags in the repository tunnel and then stored in the Bentonite Laboratory at Äspö.

³ Plastic/aluminium/plastic.



Figure 1-2. End result of stitch drilling around the copper electrodes in bentonite block C4 and uplift of the released smaller bentonite block.

2 Experimental

It was decided to start the post-test examination by removing copper electrode “Black” from the retrieved bentonite block. However, before doing so final electrochemical measurements were performed on all three electrodes.

2.1 Final electrochemical measurements

The final electrochemical measurements comprised measurements of the corrosion potential and also electrochemical impedance spectroscopy (EIS). Here the corrosion potentials measured for electrode “Black” are given as a back-up for the post-test examination of the electrode. Real-time corrosion monitoring with the SmartCET[®] instrumentation, as performed at Äspö before retrieval and also intended for the final measurements, turned out to be impossible; the corrosion potentials of the copper electrodes had now drifted apart too much.

The package with the retrieved bentonite block containing the copper electrodes was brought to Clay Technology in Lund on November 14. It was placed in the laboratory over night and opened the following morning to allow for the final measurements. Two reference electrodes and a thermometer were installed in the bentonite block as shown in Figure 2-1. Holes were drilled in the bentonite block to a depth of about 5 cm and some Äspö groundwater was poured into the holes before placing the reference electrodes in the same. The measurements were then performed in the following order:

- The corrosion potentials of the three electrodes were followed during 20 min with a measuring frequency of 1 Hz.
- The EIS measurements performed on 2011-09-09 at Äspö were repeated.
- The corrosion potential of electrode “Black” was monitored over night with a measuring frequency of 0.1 Hz⁴.

Recorded corrosion potentials relative the used silver-silver chloride reference electrode were converted to mV SHE. The temperature in the bentonite block was 17°C.

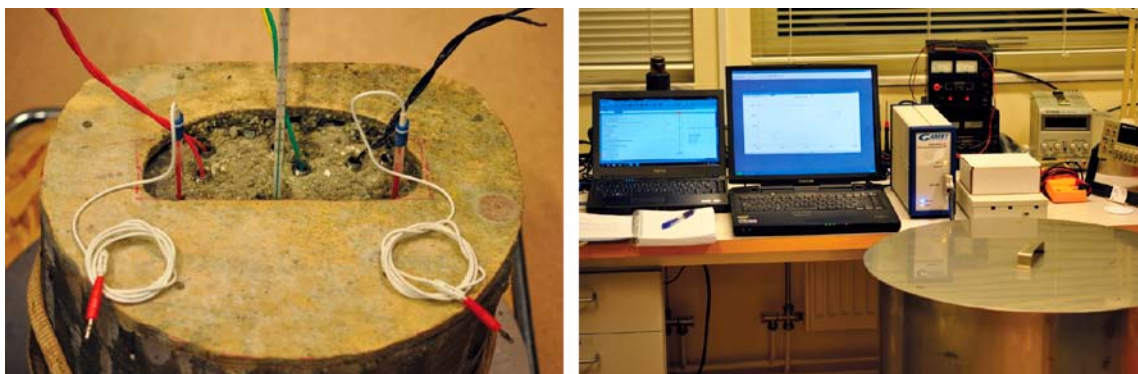


Figure 2-1. Experimental set-up for final electrochemical measurements. (Left) Top of the retrieved bentonite block with its electrode leads to the copper electrodes and two installed reference electrodes with a thermometer in between, (right) the retrieved bentonite block with its electrodes placed in a Faraday's cage (lower right in the picture).

⁴ This replaced the intended real-time corrosion monitoring with SmartCET[®] instrumentation that turned out to be impossible to perform.

Thus the corrosion potential of each copper electrode from dh 5 has been measured on three occasions. These are:

- Immediately after part of the concrete plug to the outer section had been removed (2011-02-04).
- After the back-fill in the deposition tunnel had been removed and about a week before retrieval of the small bentonite block containing the copper electrodes (2011-09-09/12).
- Just before removing copper electrode “Black” from the retrieved bentonite block (the present work on 2011-11-15/16).

The measurements described above were performed with the very same equipment and in about the same way, the only differences being position of reference electrodes and length of measurements.

2.2 Removal of electrode

On November 16 copper electrode “Black” was removed from the small bentonite block. By means of a narrow chisel deep vertical trenches were made in the bentonite block and a few bentonite pieces were broken loose as shown in Figure 2-2. A loose bentonite piece was immediately stored in double evacuated tri-laminate bags and placed in a glove-box. In this way two fairly large bentonite pieces were broken loose and stored. Finally a third smaller piece was broken loose after which the copper electrode could be removed from the bentonite block. One of the photographs in Figure 2-3 shows the copper electrode still in place in the bentonite block after removal of the three bentonite pieces, and the other shows the electrode during removal from the bentonite block. (After the copper electrode had been removed, the bentonite block with the remaining two copper electrodes was again sealed in its tri-laminate bags.)

When the electrode had been removed from the bentonite block, it was first visually examined and its appearance documented by a series of photographs. Then it was cut in a number of samples for further examination.

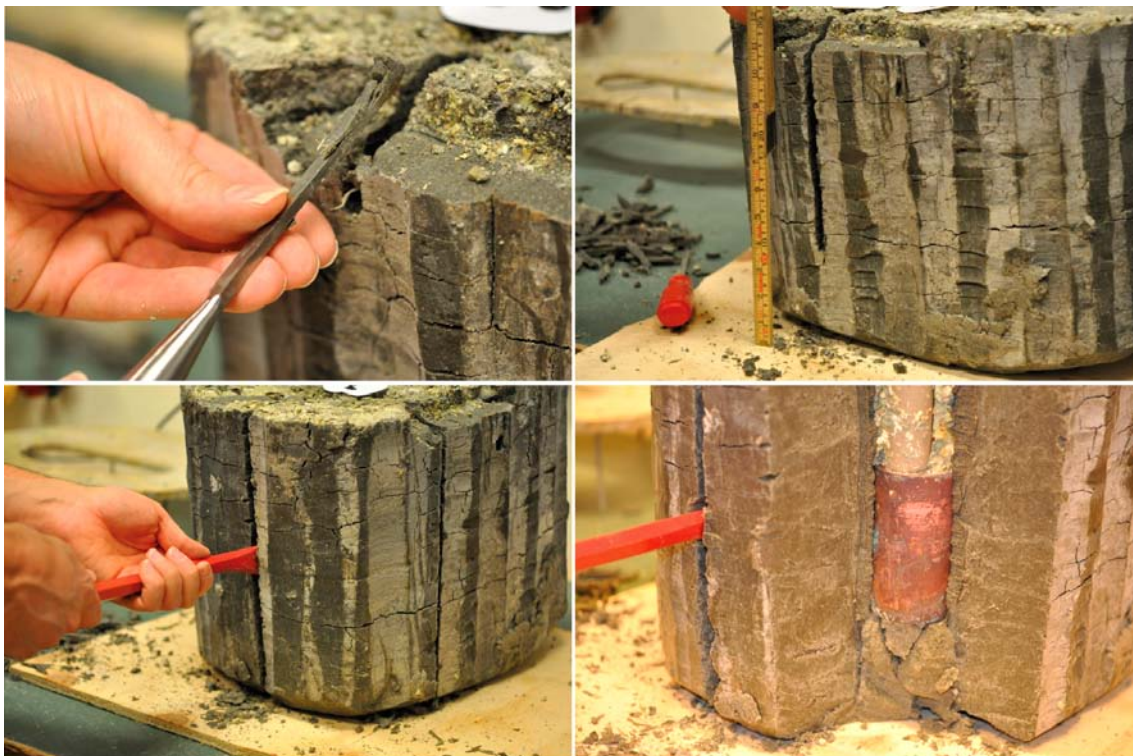


Figure 2-2. Procedure used for removal of the copper electrode from the small bentonite block. Vertical trenches were first made in the bentonite block by means of a chisel, and then bentonite pieces were broken free in the way shown in the figure. (Flashlight was unfortunately used for the lower right figure.)



Figure 2-3. Removal of the copper electrode from the bentonite block. (Left) The copper electrode just about to be removed, and (right) being removed from the bentonite block.



Figure 2-4. (Left) Cutting out samples from the copper electrode, and (right) temporary storage of samples from the copper electrode.

Samples were cut from the copper electrode in the following way. The copper electrode was first tightly fastened in a vice, see Figure 2-4, and then a horizontal cut was made by a handsaw and step by step vertical cuts were made to release samples of suitable size. (The sides of the copper electrode, that of necessity were damaged, were later picked for sampling of corrosion products.)

2.3 Identification of corrosion products

X-ray diffraction (XRD) measurements, Fourier transform infrared (FTIR) spectroscopy, and Raman spectroscopy have been employed to identify corrosion products on the copper electrode.

Corrosion products for XRD measurements and FTIR spectroscopy were scraped off from two areas of the copper electrode surface, see Figure 2-5; one that contained mainly brownish corrosion products, and another that also contained blue-green corrosion products. FTIR and Raman spectroscopy have also been applied on corrosion products remaining on the electrode surface.

For the XRD measurements a PANalytical X'Pert PRO powder diffractometer was used with Cu-K_α radiation ($\alpha_1 + \alpha_2$) in reflection mode. The evaluation was performed with the PANalytical HighScore Plus software linked with an ICDD⁵ powder database. The evaluation procedure also involved comparing the obtained spectra with a spectrum for bentonite, since bentonite is present in the scrapings, and with reference spectra for different copper corrosion products.

⁵ International Centre for Diffraction Data.



Figure 2-5. The two photographs show where corrosion products were scraped off from the copper electrode. (Left) Sample area H with mainly brownish and (right) sample area V with also blue-green corrosion products.

FTIR spectroscopy was performed on corrosion product scrapings from the two areas on the copper electrode, see above, and also on corrosion products that still remained on the electrode surface. The following methods have been applied:

- KBr transmission analysis,
- FTIR microscopy, and
- ATR⁶-FTIR analysis directly on the surface.

For the measurements a Biorad FTS 175 C spectrometer equipped with a UMA 500 microscope was used. The ATR-FTIR and KBr transmission spectra were recorded using a DTGS (deuterated triglycine sulphate) detector in the range from 230 to 4,000 cm^{-1} , while a MCT (mercury cadmium telluride) detector with a low wave number cut-off of 430 cm^{-1} was used for the FTIR microscopy. All spectra were recorded using a resolution of 8 cm^{-1} .

The Raman spectroscopy was performed on corrosion products that remained on Samples 3 and 6. The Raman spectra were obtained by using a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer coupled to an Olympus BXFM optical microscope. The measurements were performed using a 514 nm laser excitation line, a 50x objective with a long working distance, and a 600 grooves/mm grating, which gave a spectral resolution of approx. 2 cm^{-1} /pixel. The power at the samples was set to 0.14 mW in order not to destroy the corrosion products. A multi-channel air-cooled CCD⁷ detector was used, with integration times of between 20 and 35 s. The spectra are presented without baseline correction.

2.4 Microscopy

A USB microscope⁸ has been used to examine the surface on the copper electrode (seen in Figure 2-5) at a magnification of about 50x. Some areas were also viewed at a higher magnification. Scanning electron microscopy has been used to examine areas of the surface in more detail.

A Nova 600 NanoLab DualBeam™ SEM/FIB instrument has been used to prepare a few “micro cross-sections” through the electrode surface by means of focused ion beam milling to examine and characterize the corrosion product layer on the electrode.

⁶ Attenuated total reflectance.

⁷ Charge-coupled device.

⁸ Dino-Lite Pro HR digital microscope.

3 Results and discussion

Below the appearance of the copper electrode after it had been freed from the small bentonite block is presented first, followed by information from the identification of corrosion products, and the results from the performed electrochemical measurements. Based upon the gathered information a scenario of exposure is finally given.

3.1 Appearance of electrode after exposure

It was obvious from the appearance of the copper electrode, when part of the surrounding bentonite had been removed, see Figures 2-2 and 2-3, that both Cu(I) and Cu(II) corrosion products existed on the electrode surface. The blue-green Cu(II) corrosion products were not evenly distributed on the surface; they were more abundant on part of the electrode. Corrosion products were also found on the adjacent bentonite after removal of the copper electrode from the bentonite block, see Figure 3-1, thus revealing a better adherence to the bentonite on part of the surface. A series of photographs was taken of the electrode after it had been removed from the bentonite block, and four are seen in Figure 3-2. Close-ups from a few places on the electrode are shown in Figures 3-3 through 3-5. In Figure 3-4 both exposed and non-exposed areas on the top surface of the copper electrode are shown – the latter were covered by the PEEK distance pieces seen in Figure 2-3.

The appearance of the copper electrode reminds of the coupons from the LOT test parcels (Karlund et al. 2009), but is different from the appearance of the surface on full-size canisters (Taxén et al. 2012). For the latter blue-green Cu(II) products have only been observed on one or a few single spots from visual examination immediately after removing the surrounding bentonite. Differences that can have a marked influence on the corrosion behaviour between the exposed small samples and the big components exist. The most convincing is that lubricants were used in manufacturing of the full-size bentonite blocks and rings (so available machines could handle the required pressure); lubricants have not been used for the copper electrodes in the Prototype Repository, nor for the copper coupons in the LOT test parcels. The surface of the electrode is shown in more detail in Figure 3-6. The machining marks are visible and part of the corrosion product film seems missing. It might have been lost during the removal of the electrode from the bentonite block. Micro cross-sections through the corrosion product layer on the electrode surface are shown in Figure 3-7. Both figures reveal that the corrosion product layer appears quite uneven and porous.

No unmistakable signs of pitting have been found.



Figure 3-1. Corrosion products still remaining on adjacent bentonite after removal of the electrode.

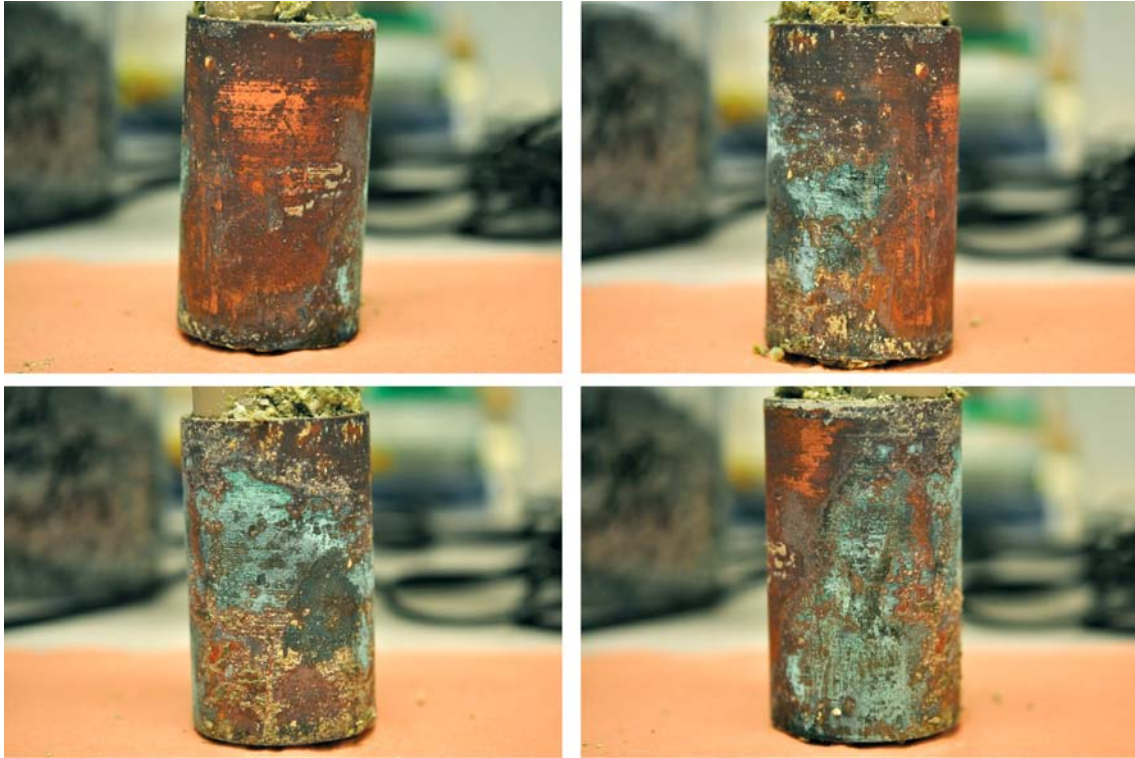


Figure 3-2. Appearance of copper electrode "Black" immediately after removal from the bentonite block.

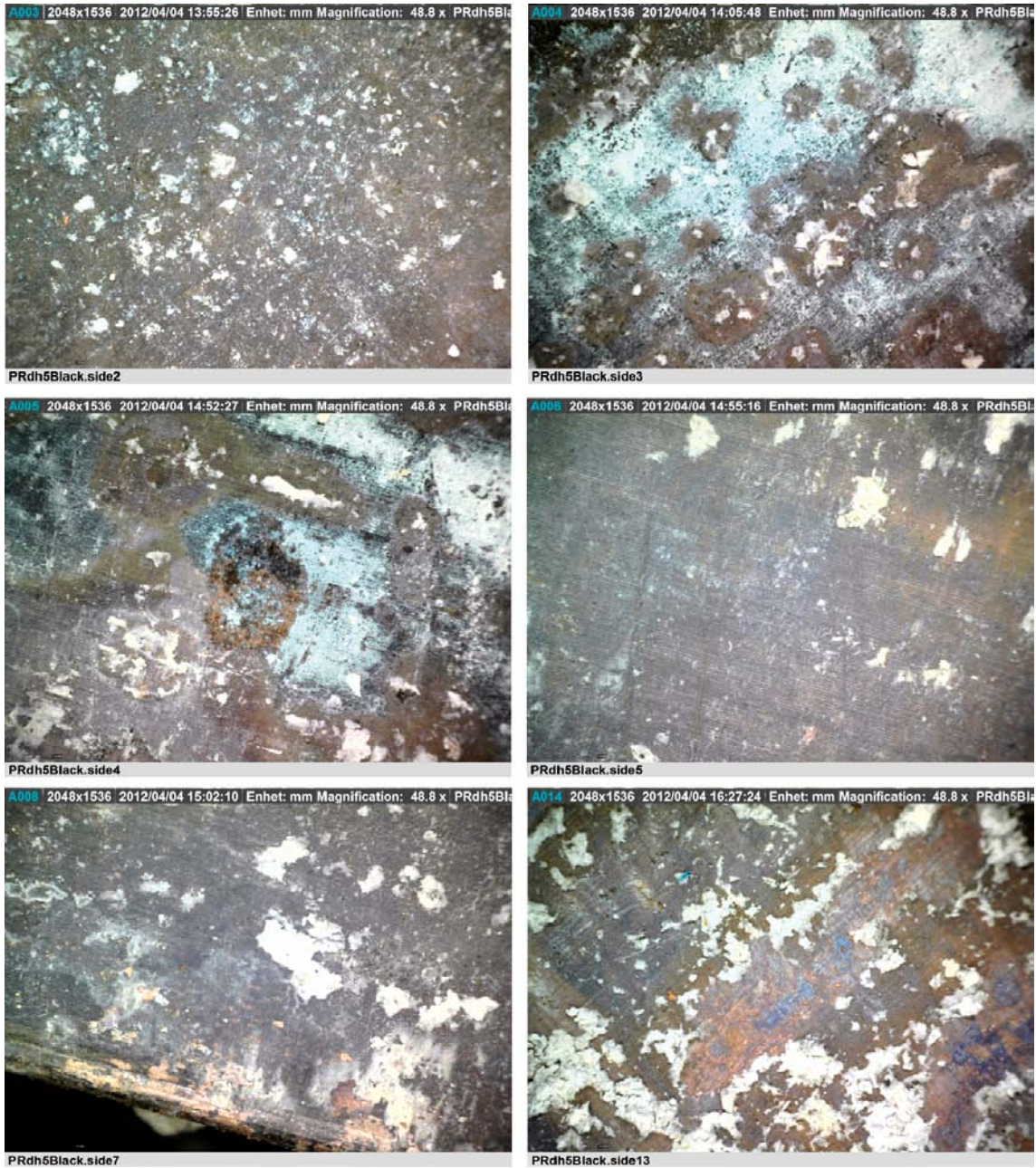


Figure 3-3. Close-ups from the cylindrical vertical surface of the copper electrode after exposure. The whitish remains on the surface in the pictures are bentonite. (magnification about 50x).

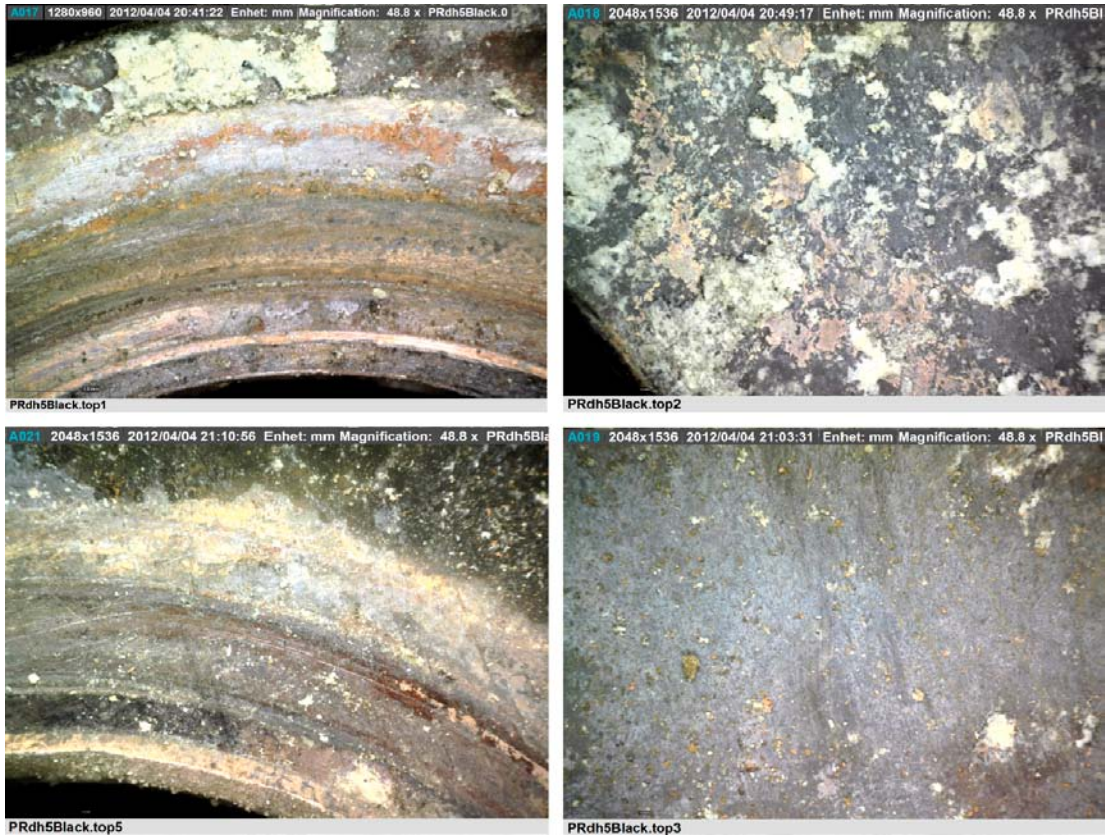


Figure 3-4. Close-ups from the top surface of the copper electrode after exposure. Part of the surface in the left pictures has been covered by PEEK distance pieces. (magnification about 50x).

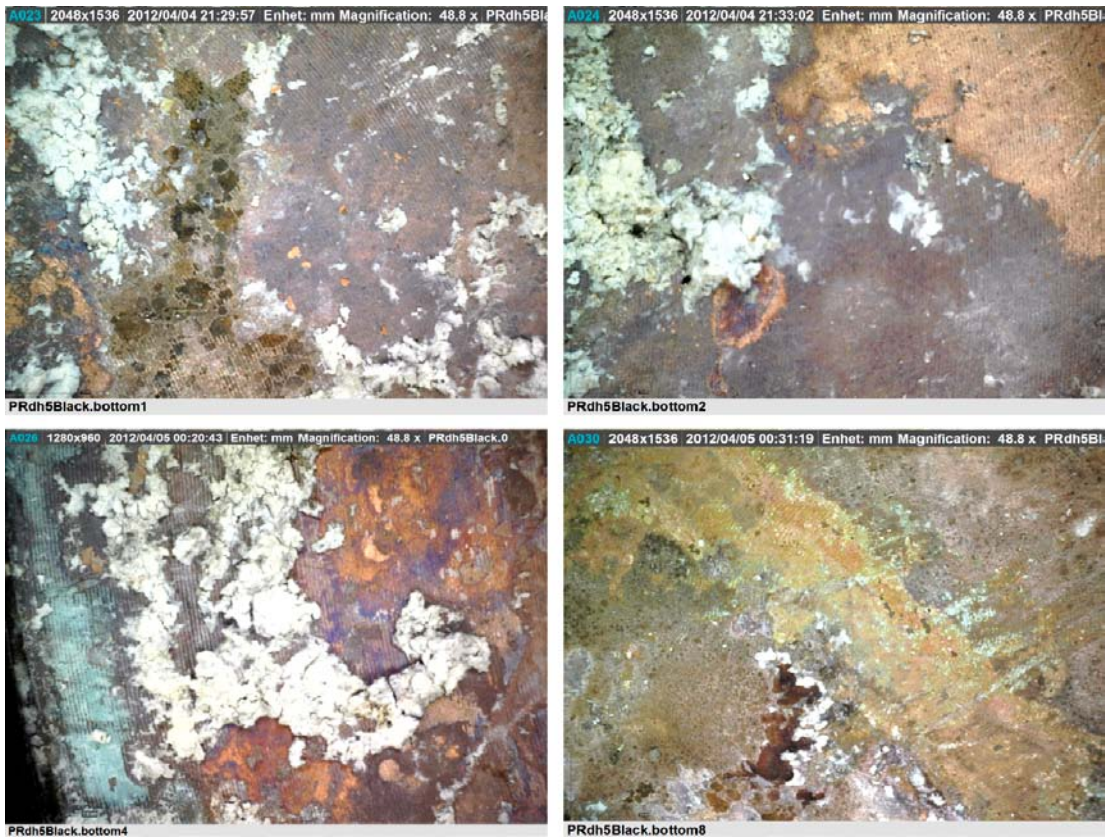


Figure 3-5. Close-ups from the bottom surface of the copper electrode. (magnification 50x).

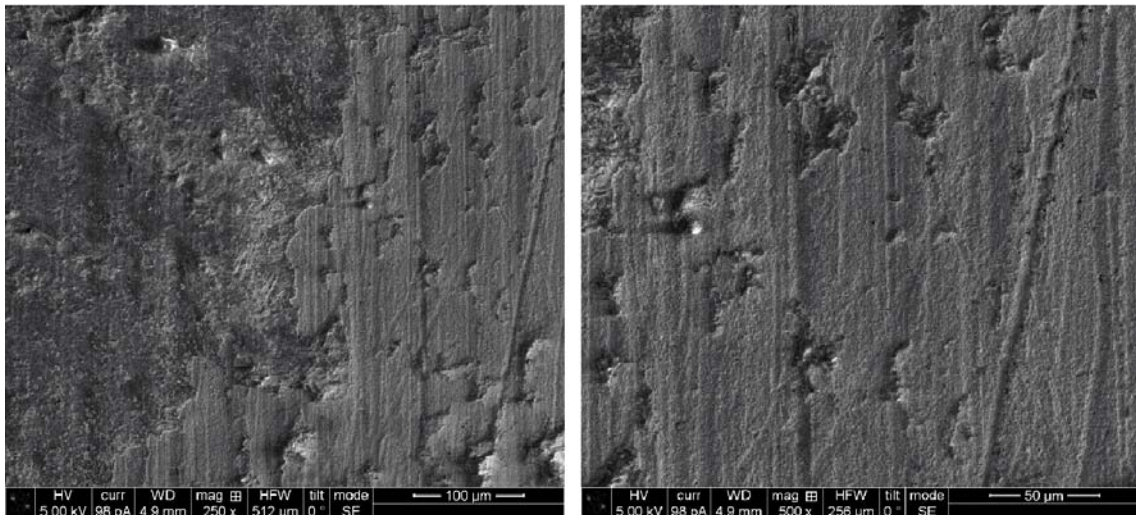


Figure 3-6. The surface of the copper electrode in higher magnification (sample 4; SEM). (magnification left 250x and right 500x).

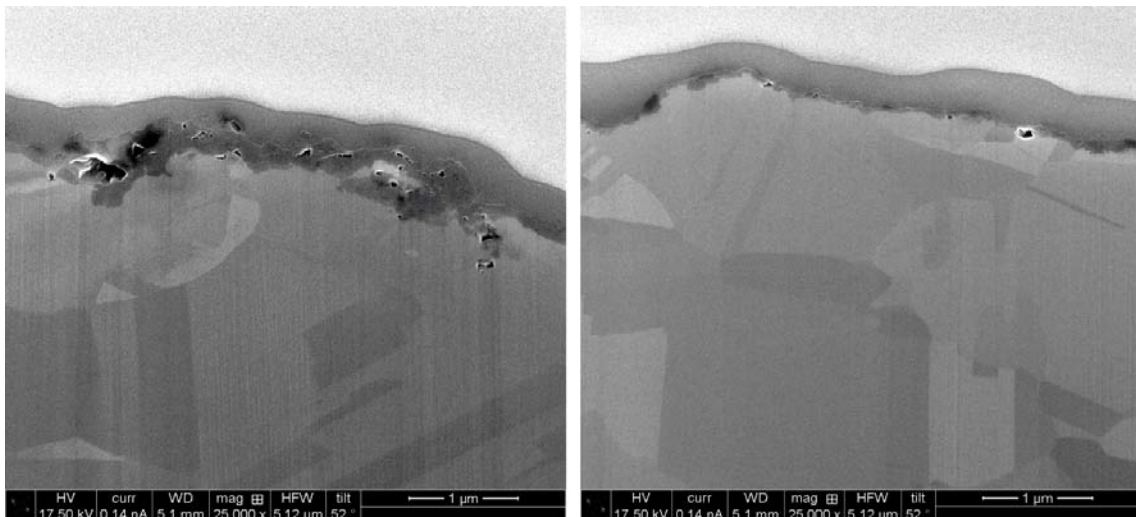


Figure 3-7. Micro cross-sections from the copper electrode (SEM/FIB microscopy; sample 4). (The quite irregular dark-grey area in between the two platinum deposits on top, one grey and one pale-grey, and the copper metal below constitutes the corrosion product layer.) (magnification 25,000x).

3.2 Corrosion products

As soon as the first bentonite piece had been broken loose from the bentonite block and the copper electrode surface was seen, it was obvious that both Cu(I) and Cu(II) corrosion products had been formed during the exposure. The XRD measurements verified the presence of cuprite, Cu_2O , and malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$, see spectra in Figure 3-8; paratacamite, $\text{Cu}_2(\text{OH})_3\text{Cl}$, was not found contrary to findings from copper coupons in LOT test parcel A2 (Karnland et al. 2009). However, while the pore water of the bentonite in dh 5 from start of exposure was dominated by tap water (Johannesson 2002), the supply of Äspö groundwater was abundant for the LOT test parcels (Karnland et al. 2009).

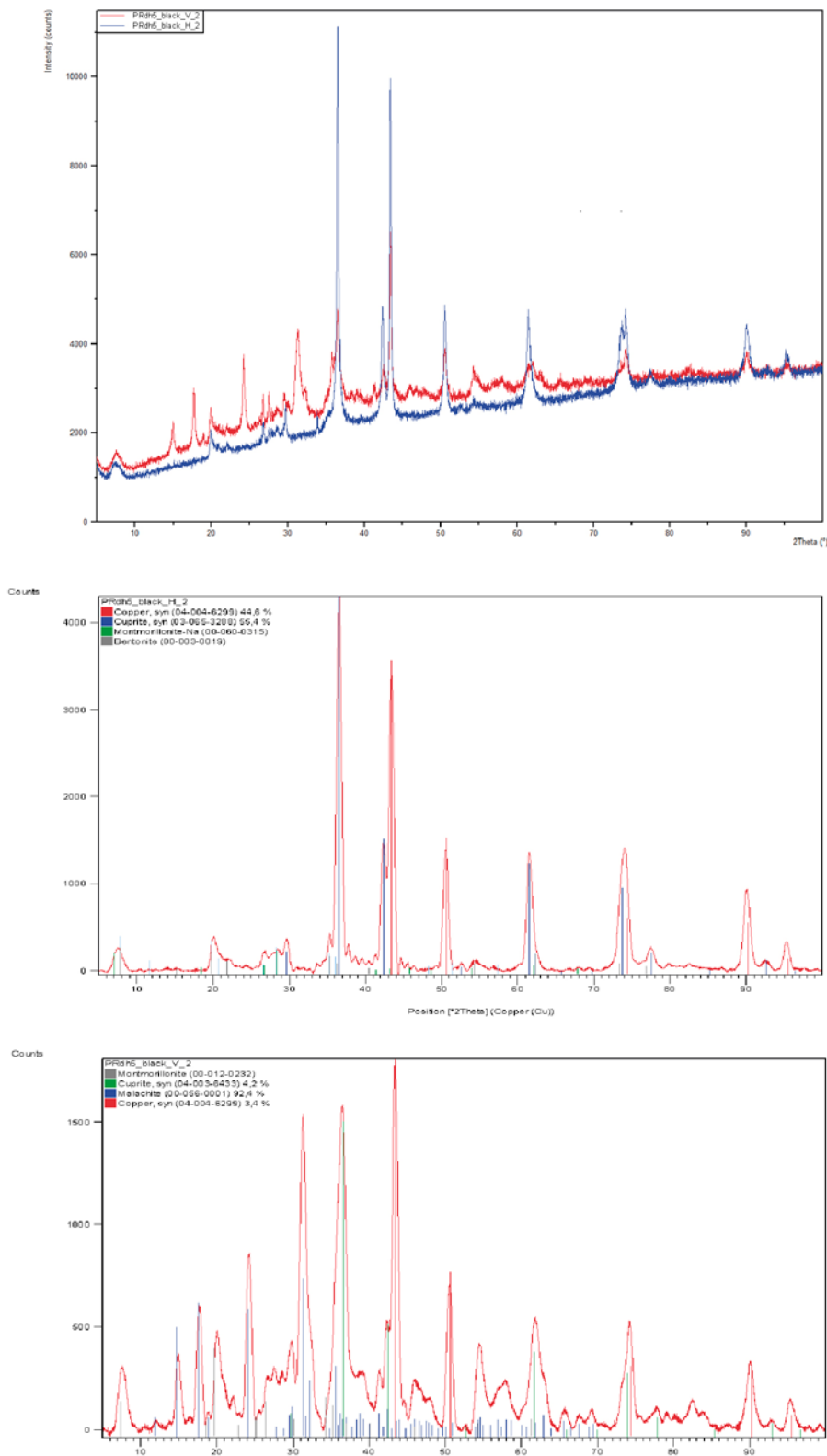


Figure 3-8. XRD spectra from corrosion products scraped off from two areas on the copper electrode marked H and V. (top) Combined diagram, (middle) spectrum from area H, and (bottom) spectrum from area V.

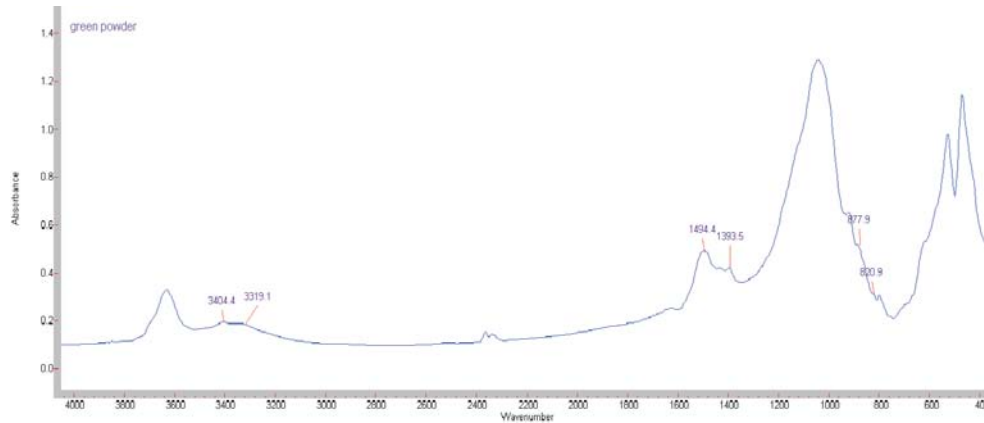


Figure 3-9a. FTIR transmission spectrum from Sample V with blue-green corrosion products. (Peaks from malachite are marked with their wave numbers.)

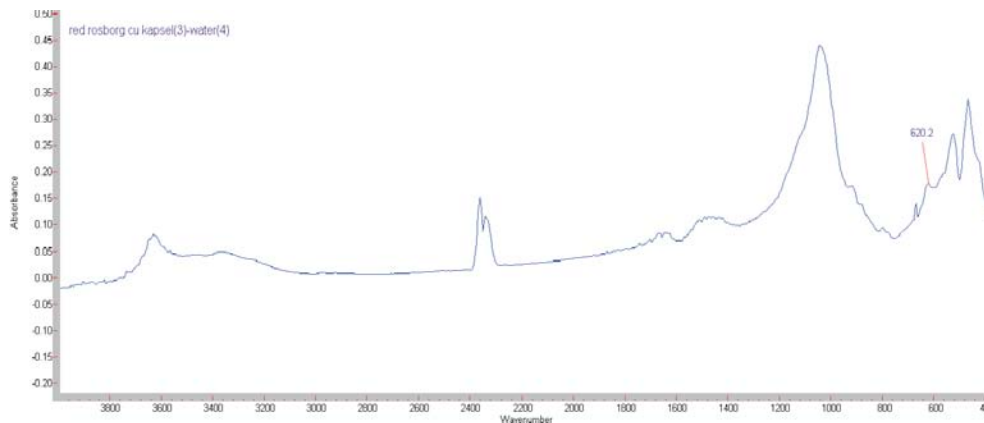


Figure 3-9b. FTIR transmission spectrum from Sample H with brownish corrosion products. (A peak that most probably originates from cuprite is marked with its wave number.)

The performed FTIR and Raman spectroscopy confirmed these observations. The FTIR spectra from the KBr transmission measurements on corrosion products from sample areas V and H are shown in Figures 3-9a and 3-9b respectively. The spectra are dominated by bands from bentonite (strong bands from Si-O vibrations at 1,000–1,100 cm^{-1} and OH bands at 3,600 cm^{-1}), but the spectra have also bands from malachite and cuprite. Malachite was present in the blue-green corrosion products. Malachite has also been identified by means of reflection measurements on selected places on top of the electrode, see example in Figure 3-10. For Raman spectra verifying the presence of malachite and the (most probable) absence of paratacamite, see Figure 3-11.

3.3 Corrosion potential

Just before cutting loose the copper electrode from the small bentonite block the corrosion potential of the electrode was as high as 165 mV SHE, see the potential-time plot (for 2011-11-15) in Figure 3-12. As a comparison the corrosion potential was –40 mV SHE (2011-02-04) when part of the concrete plug to the outer section had been removed and 25 mV SHE (2011-09-12) about a week before retrieval of the small bentonite block with the electrodes from the upper bentonite block in dh 5.

The reason for the different corrosion potentials in February and September is not anticipated to be due to ingress of air to the copper electrode after opening of the outer section and removal of the back-fill, but rather due to an adaptation to changes in the near-field environment caused by the relief of pressure.

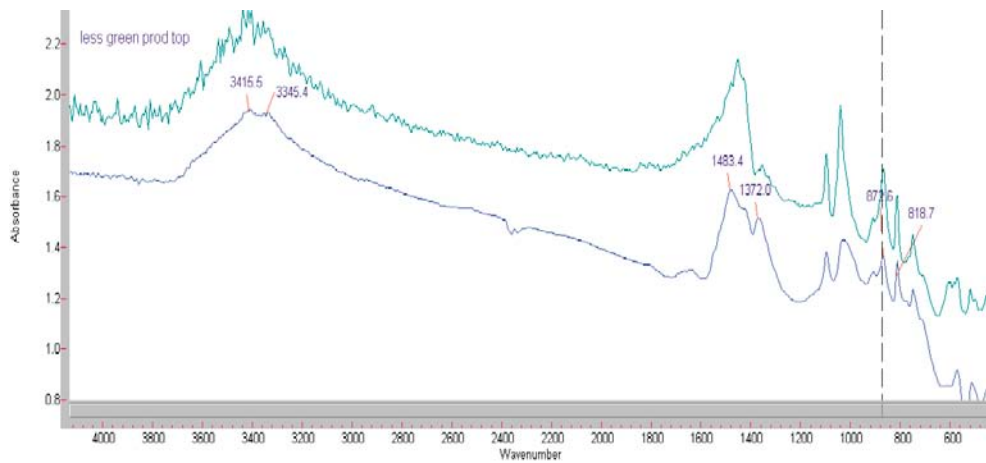


Figure 3-10. FTIR reflection spectra taken with a FTIR microscope from blue-green corrosion products on two places on top of the copper electrode seen in Figure 7.

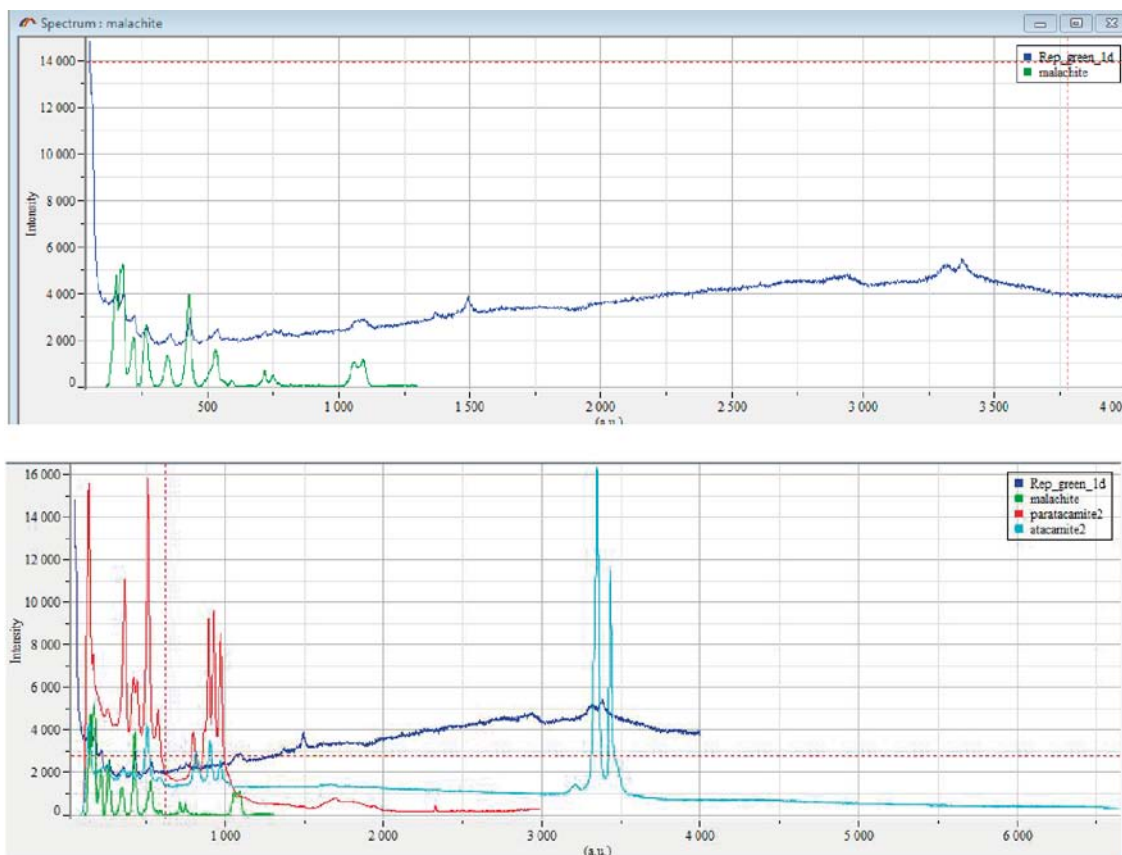


Figure 3-11. Raman spectra verifying the presence of malachite.

The electrode/bentonite interface has to establish a new steady-state and in doing so a higher corrosion potential was obtained. However, the considerably higher corrosion potential measured in November is anticipated to be due to air ingress to the interface in spite of the effort done to protect the retrieved bentonite block from air exposure during retrieval and storage. Immediately after uplift on September 20 the small bentonite block with the copper electrodes was packed in triplicate evacuated tri-laminate bags that were not opened until November 15 for the final electrochemical measurements.

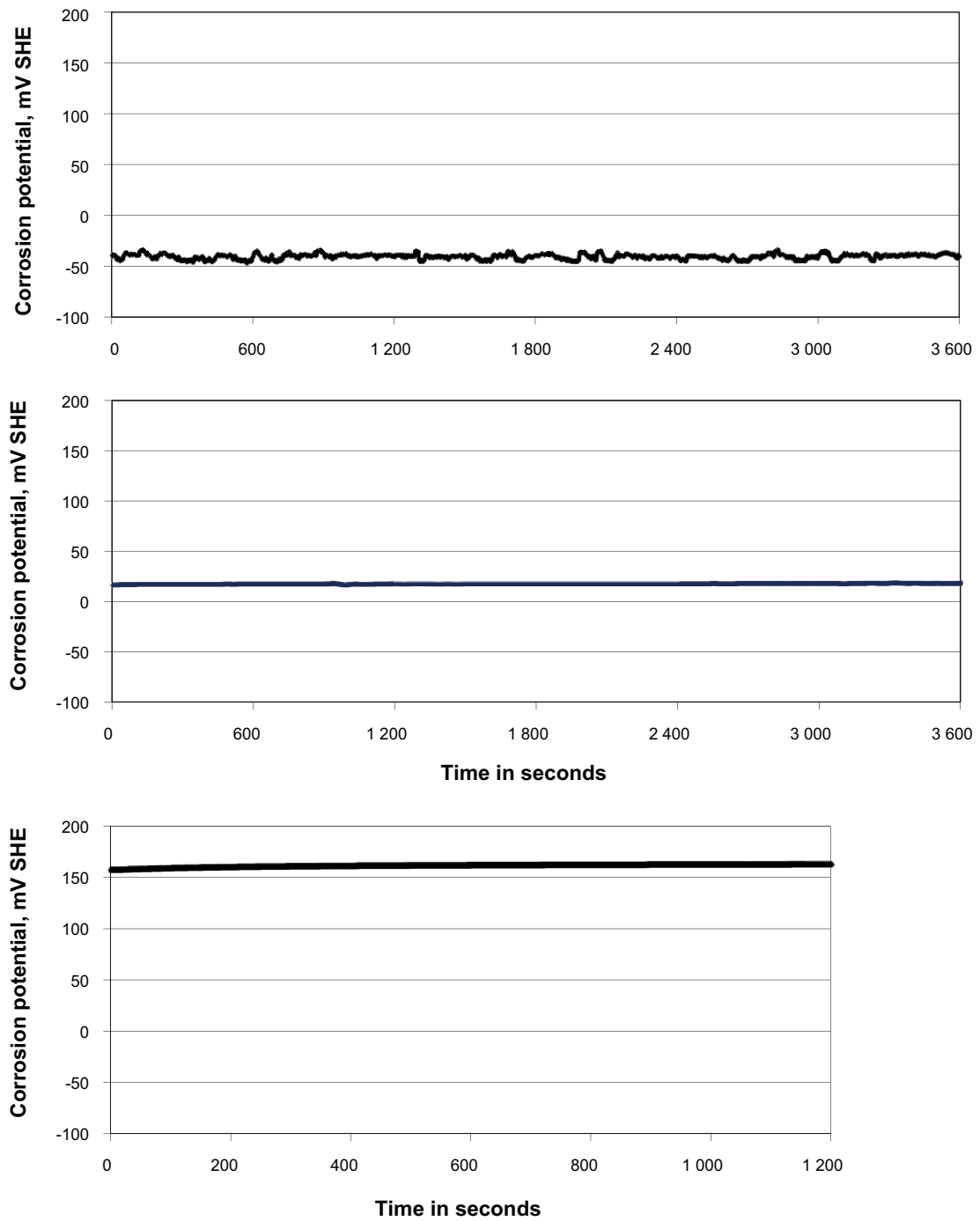


Figure 3-12. The corrosion potential of copper electrode “Black” on three occasions during 2011: (top) 2011-02-04, (middle) 2011-09-12, and (bottom) 2011-11-15.

The corrosion potential of the copper electrode merely increased by 6 mV over night from November 15 to the next day; thus, an abrupt change of well over 100 mV in a few hours after opening the tri-laminate bag on November 15 is not expected. Most likely the air ingress occurred during retrieval of the bentonite block. (In Figure 2-2 cracks are seen in the bentonite block below the copper electrode. However, it is not certain if these were formed during the removal of the copper electrode, or if they were already present from the retrieval of the small bentonite block.)

In Table 3-1 the measured corrosion potentials for the copper electrode are compared with corrosion potentials obtained for a pre-exposed and also for a newly installed copper electrode in the bentonite test package that was set up after retrieval of LOT test parcel A2 in January 2006 (Rosborg and Pan 2008). Oxidic conditions prevailed in the bentonite test package.

It is of course unfortunate that the corrosion potential of the copper electrode from the Prototype Repository is not known all through the exposure – experimental risks and difficulties have upset this. Thus, the only known for certain corrosion potential of the copper electrode during exposure, all the way from installation up to opening of the outer section, is the one measured immediately after penetration of the concrete plug; all other corrosion potentials have to be anticipated based on experience and findings.

Most likely the corrosion potential has first increased after installation, not necessarily immediately but after a while, and findings of blue-green Cu(II) corrosion products is considered a proof of that. After reaching a maximum the corrosion potential has then gradually decreased to the measured value of –40 mV SHE. It is reasonable to believe that the corrosion potential has not been lower than the –40 mV SHE measured on 2011-02-04. Thus, it is anticipated that the copper electrode has been exposed to oxidic conditions all through the exposure period. (*Comment: Alternatively the surrounding electrolyte was reducing but the kinetics for reducing the corrosion products on the copper surface are slow and the corrosion potential has halted at the measured value.*)

Since the blue-green corrosion product was found to be malachite and not paratacamite, this could mean that malachite was formed quite early during the exposure, when the chloride activity was still fairly low. It is anticipated that the chloride activity increased considerably when the drainage to the Prototype Repository was closed in November 2004.

(Comment: The corrosion potential of the copper electrode has been fairly high at least twice: first early during the exposure, and then after retrieval of the small bentonite block. The first is anticipated and the latter is a fact – the corrosion potential was measured on 2011-11-15. Thus, hypothetically malachite could have been formed on the later occasion and not on the first. However, paratacamite rather than malachite had been expected when the saline groundwater dominate the pore water.)

Table 3-1. Comparison with corrosion potentials measured in the bentonite test package.⁹

Electrode	Pre-exposure	Corrosion potential in mV SHE		
		2011-02-04	2011-09-12	2011-11-15
PRdh5Black	8 years	–40	25	165
LOTA2btpBlue	6 years	1 week after retrieval 109 mV SHE		
ditto		2 months after retrieval 195 mV SHE		
LOTA2btpCu1	–	1 day after installation 44 mV SHE		
ditto		2 months after installation 164 mV SHE		

⁹ btp denotes the bentonite test package that was formed by molding a bentonite block consisting of bentonite rings 35, 36 and 37 from LOT test parcel A2 in paraffin after retrieval in January 2006; the copper electrode LOTA2btpBlue had been pre-exposed in bentonite ring 36 for six years and the electrode LOTA2btpCu1 was installed in the bentonite test package five months after retrieval of the test parcel.

3.4 Scenario of exposure

Based upon results from corrosion potential measurements and findings from the post-test examination the following scenario of exposure for the copper electrode in the outer section of the Prototype Repository is likely:

- *Start:* Between manufacturing and installation of the copper electrode in the upper bentonite block of dh 5, it has only been exposed to air at ambient conditions. Thus, when installed the copper electrode had merely a very thin adherent cuprite film on the surface. The bentonite block had been conditioned with tap water to a water ratio of 17.5%, thus the pore water early in the exposure had a fairly low chloride content.
- After some length of exposure a corrosion potential was reached that allow formation of Cu(II) corrosion products. When this happened the chloride activity was still fairly low since malachite rather than paratacamite was formed.
- In November 2004 when the drainage of the Prototype Repository was temporary closed, it is known that the “electrochemical activity” on the copper electrode was increased from a very low to a much higher value. This increase must be due to a change in the near-field environment, most probably an increased wetting of the bentonite block with groundwater; it is anticipated that the pore water from now on so to say is dominated by the saline groundwater in the surrounding rock rather than by the tap water. Quotation from (Goudarzi and Johannesson 2005, p 38):
“The processes have been slow up to about 20 days after the drainage of the tunnel was closed. Very small changes of the measured parameters have occurred up to that date. After that the readings from some of the total and pore pressure sensors placed in the buffer have reacted strongly (quick increase in pressure).”
- Due to the closure the chloride content of the pore water has most probably increased considerably. Since paratacamite was not observed on the electrode surface after exposure, it is anticipated that the corrosion potential already before the closure has decreased to a value where Cu(II) corrosion products could not form.
- Later on the corrosion potential has declined even further, influenced by changes in the near-field environment and filming of the surface, and reached a corrosion potential of -40 mV SHE at the time when the concrete plug to the outer section was removed.
- *End:* In the end of exposure the copper electrode had both copper (I) and copper (II) corrosion products on its surface and the corrosion potential was -40 mV SHE. Thus, the near-field environment can be considered mildly oxidizing.

4 Conclusions

The outer section of the Prototype Repository at the Äspö Hard Rock Laboratory has been opened. The present report describes the findings from exposure of a copper electrode during eight years in the upper bentonite block of deposition hole 5 where the temperature has been somewhat below 35°C. The post-test examination and the performed electrochemical measurements have revealed the following:

- Both Cu(I) and Cu(II) corrosion products were found on the copper electrode; the presence of cuprite and malachite was identified by both XRD measurements, and FTIR and Raman spectroscopy.
- The corrosion potential of the electrode has first increased and reached a maximum (most probably before November 2004) and then decreased to the measured value of -40 mV SHE at the time for opening of the outer section of the repository.
- The near-field environment was still after eight years exposure mildly oxidising.

No unmistakable signs of pitting have been found on the electrode.

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Name	Affiliation	Contribution
Stefan Grandin Svårdh	SKB Äspö HRL	Information
Lars Göthe	Stockholm University	XRD
Lars-Erik Johannesson	Clay Technology AB	Information
Ola Karnland	Clay Technology AB	Information
Tadeja Kosec	ZAG, Ljubljana	Raman spectroscopy
Viljem Kuhar	ZAG ¹⁰ , Ljubljana	Microscopy
Karin Nilsson	SKB Äspö HRL	Information
Ulf Nilsson	Clay Technology AB	Cutting of bentonite block
Siv Olsson	Clay Technology AB	Information
Dan Persson	Swerea KIMAB AB	FTIR spectroscopy
Anastasia Riazanova	KTH Royal Institute of Technology	Electron microscopy

¹⁰ The Slovenian National Building and Civil Engineering Institute.

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Taxén C, Lundholm M, Persson D, Jakobsson D, Sedlakova M, Randelius M, Karlsson O, Rydgren P, 2012. Analyser av koppar från prototypkapsel 5 och 6, SKB P-12-22.

Information about bentonite block C4

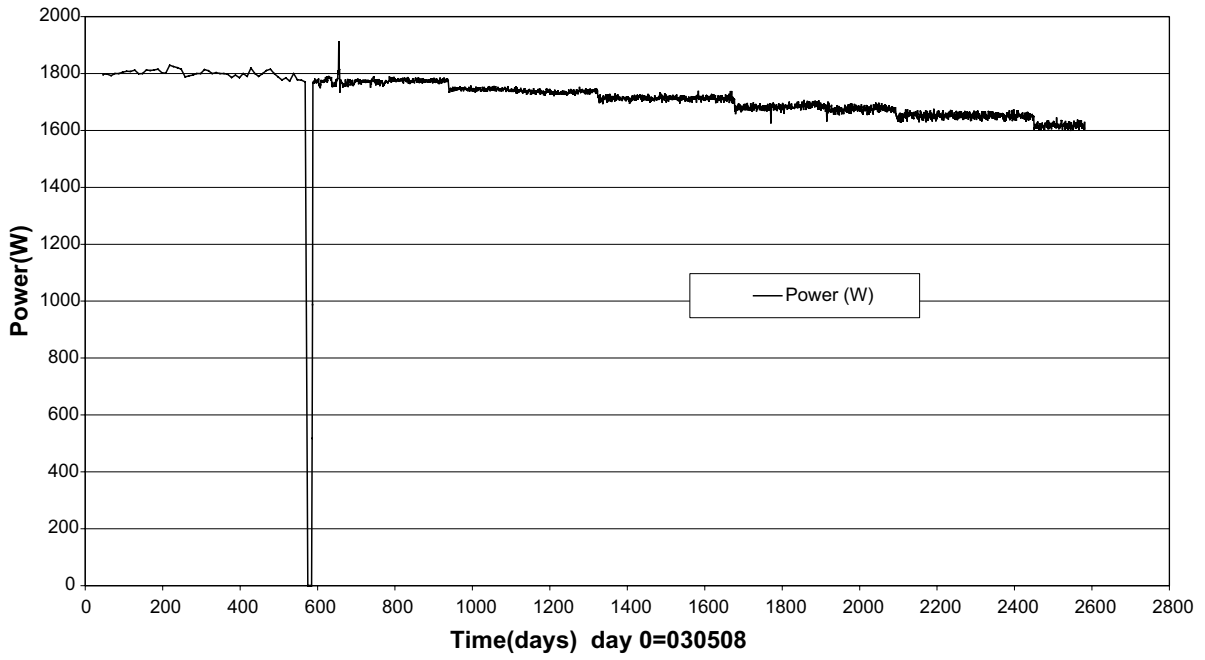
Below information about the conditioning before installation and the exposure of bentonite block C4 in the Prototype Repository is given. The photograph in the end shows where samples for post-test examination were taken from the bentonite block.

The MX-80 sodium-bentonite was conditioned with tap water to a water ratio of about 17.5% before manufacturing of blocks and rings (Johannesson 2002). The installation is described in (Johannesson et al. 2004). Thus, from start of exposure the copper electrodes were exposed to a bentonite pore water with a low chloride activity. It is anticipated that the chloride activity in the pore water soon after installation started to increase and most certainly increased considerably during and after the November 2004 closure of the drainage to the inner and outer sections of the Prototype Repository (Goudarzi and Johannesson 2005).

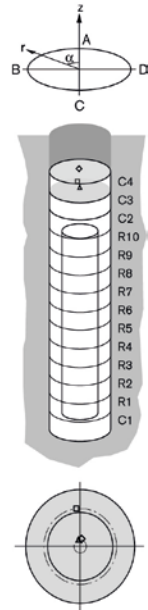
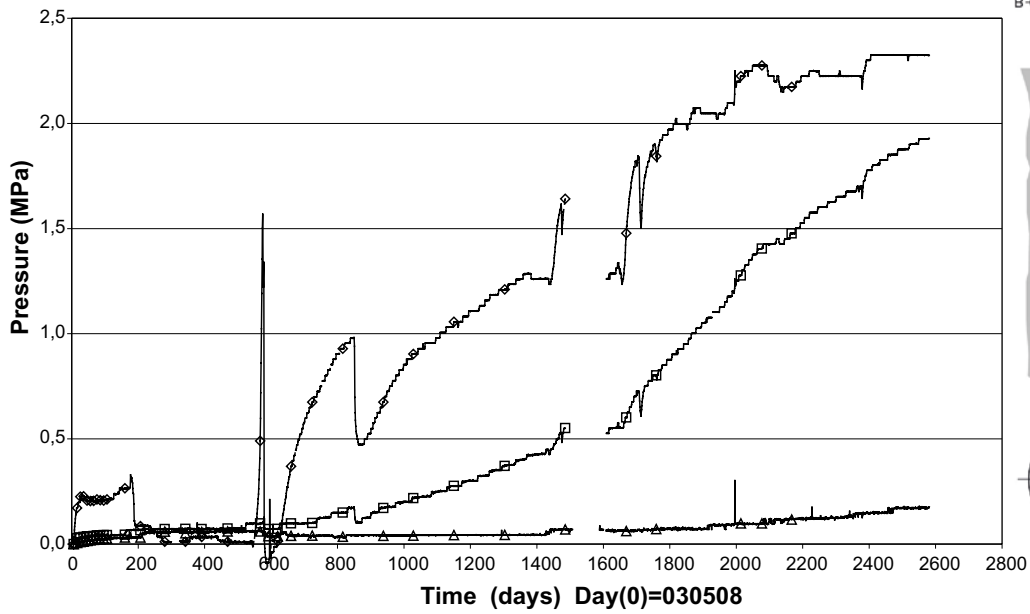
Quotation from (Goudarzi and Johannesson 2005, p 38): “The processes have been slow up to about 20 days after the drainage of the tunnel was closed. Very small changes of the measured parameters have occurred up to that date. After that the readings from some of the total and pore pressure sensors placed in the buffer have reacted strongly (quick increase in pressure). Also the total and pore pressure sensors placed in the backfill have recorded high pressures caused by the closing of the drainage. After the opening of the drainage of the tunnel, both the pore pressures and the total pressures were stabilized on a higher level than before the closing of the drainage.”

The diagrams below contain information about the conditions in dh 5 during exposure that relates to bentonite block C4.

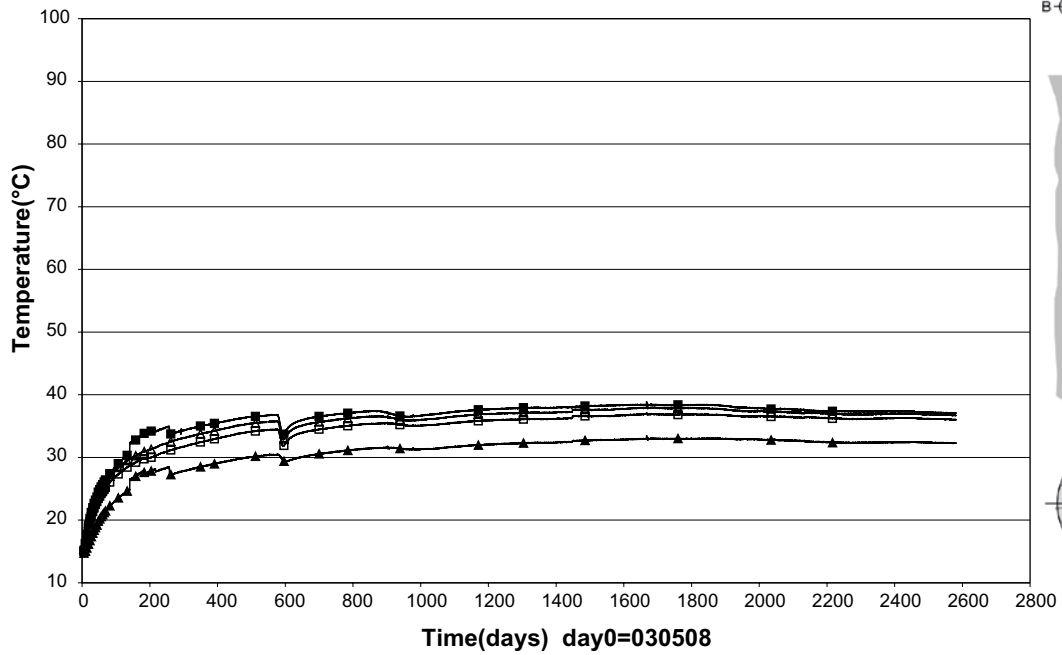
Prototype\Hole 5 (20030508-20100601)
Canister power



Prototype\Hole 5\Cyl.3 and Cyl.4 (20030508-20100601)
Total pressure - Geokon

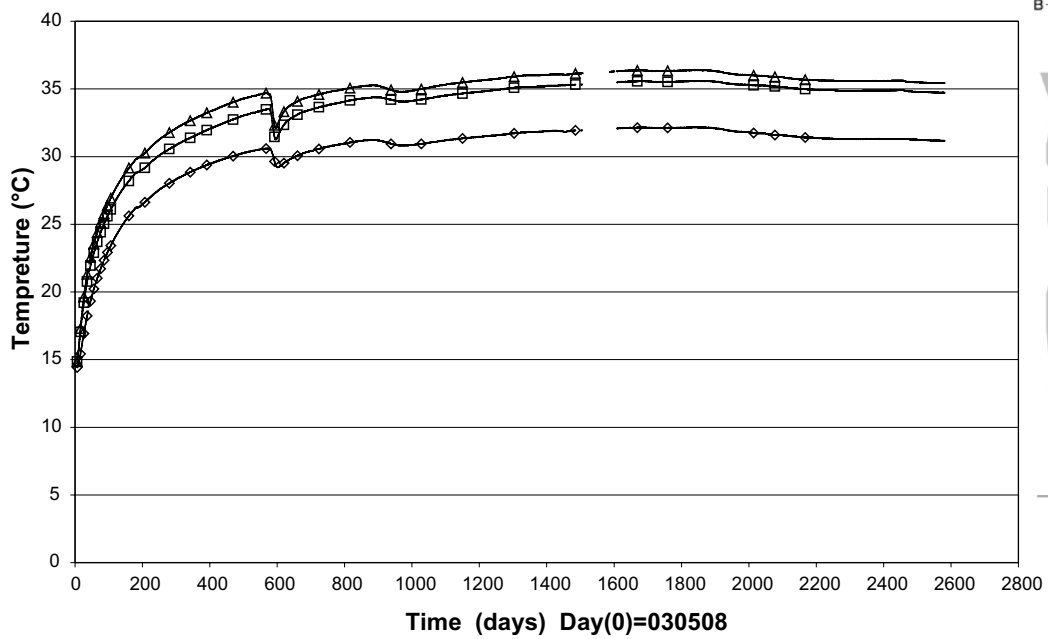


Prototype\Hole 5 \Cyl.3 and Cyl.4 (20030508-20100601)
Temperature - Pentronic



□ TB529(6.353\ 0°\0.785) △ TB530(6.353\ 95°\0.585) ■ TB531(6.353\ 185°\0.585) ▲ TB532(7.060\ 0°\0.785)

Prototype\Hole 5 \Cyl.3 and Cyl.4 (20030508-20100601)
Temperature - Geokon



△ PB525T(6.603\0°\0.100) □ PB526T(6.603\5°\0.585) ◇ PB527T(7.110\0°\0.100)

