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# EVALUATION OF SENSORS TO MONITOR THE EFFECT OF BENTONITE ON THE CORROSION RATE OF COPPER IN OLKILUOTO- TYPE SALINE GROUNDWATER

Petri Kinnunen, Timo Saario, Iva Betova

VTT Industrial Systems

In STUK this study was supervised by Jussi Heinonen and Esko Ruokola

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**Keywords:** copper, nuclear waste disposal, bentonite, corrosion sensor, reference electrode

## Abstract

This work concerns the effect of bentonite and groundwater on the corrosion of copper in a closely simulated final disposal vault environment of radioactive waste. The feasibility of two sensors—an on-line corrosion rate monitoring sensor and a modified reference electrode, has been tested with respect to Cu corrosion in MX80 bentonite saturated with highly saline groundwater in conditions closely simulating those in a nuclear waste repository. As a result, it can be stated that both sensors showed the expected stability at least up to 150 h of operation. Thus it is expected that they can be used for reliable long-term corrosion rate and electrode potential measurements in the presence of wetted bentonite. In addition, it has been demonstrated that after an initial transient period of ca. 5–8 h, Cu corrosion in bentonite saturated with highly saline groundwater becomes undetectably low probably because of the anoxic conditions reached in the free groundwater. At the same time, the corrosion potential of Cu is still in the active corrosion region according to thermodynamic calculations. Furthermore, redox potentials in the wetted bentonite remain significantly higher than in the free groundwater. This may indicate that the decomposition of the oxygen contained in the pores of the bentonite is a process occurring in a time scale larger than that of the present experiments.

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**Avainsanat:** kupari, ydinjätteen loppusijoitus, bentoniitti, korroosiosensori, referenssielektrodi

## Tiivistelmä

Tämä työ käsittelee bentoniitin ja pohjaveden vaikutusta kuparin korroosioon korkea-aktiivisen ydinjätteen loppusijoitusolosuhteita simuloivassa ympäristössä. On-line korroosionopeusanturin ja modifioidun referenssielektrodin käytettävyyttä testattiin mittaamalla kuparin korroosiota erittäin suolaisella pohjavedellä kyllästetyssä MX80-bentoniitissa olosuhteissa, jotka simuloivat tarkasti olosuhteita ydinjätteen loppusijoituspaikassa. Tulokset osoittavat, että kumpikin sensori toimii stabiilisti ainakin 150 tuntia. Siten on oletettavaa, että niitä voidaan luotettavasti käyttää pitkäaikaiseen korroosionopeuden ja elektrodipotentiaalin mittaamiseen kostutetussa bentoniitissa. Lisäksi kokeissa on osoitettu, että kokeen alussa olevan n. 5–8 tunnin transitiojakson jälkeen kuparin korroosionopeus erittäin suolaisella pohjavedellä kyllästetyssä bentoniitissa pienenee alle havaitsemisrajan johtuen pohjavedessä vallitsevista hapettomista olosuhteista. Kuitenkin termodynaamisten laskujen perusteella kuparin korroosipotentiaalin pitäisi olla ko. olosuhteissa aktiivisella alueella. Lisäksi hapetus-pelkistyspotentiaalit ovat kostutetussa bentoniitissa huomattavasti korkeammat kuin vapaassa pohjavedessä. Tämä saattaa johtua siitä, että bentoniitin huokosissa oleva happi hajoaa pidemmällä aikavälillä kuin mitä tässä työssä tehdyissä kokeissa käytettiin.

## Foreword

The present report describes the results obtained in the project “Evaluation of sensors to monitor the effect of bentonite on the corrosion rate of copper in Olkiluoto-type saline groundwater” which is funded by the Radiation and Nuclear Safety Authority, STUK. At STUK this project has been supervised by Mr. Jussi Heinonen and Mr. Esko Ruokola.

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# 1 Introduction

Deep geological repository systems constructed to dispose of radioactive wastes containing long-lived radionuclides have to satisfy strict requirements. They have to ensure that radionuclide release into the geosphere does not occur, or that it can be retarded to the extent that any radioactive dose eventually reaching the biosphere is well within the limits required for human safety. The majority of concepts suggested until now to dispose of high-level radioactive wastes adopt a near-field multi-barrier engineering system, consisting of:

- The form of the waste itself, with its inherent physical and chemical properties;
- A containment of the waste form (i.e. a metal canister);
- A bentonite buffer (e.g. compacted bentonite or mixtures of bentonite and sand) which will surround and isolate the canister from the host bedrock.

The role of metal canisters is to prevent any exposure of the waste form to groundwater, and the subsequent mobilisation and transport of radionuclides. The canisters are designed to fulfil several functions:

- to resist corrosion
- to resist pressure
- to resist thermal and radiation effects.

Experimental studies aiming at estimating the corrosion rate of the canister materials in relevant conditions should be able to take into account the exceptionally long time period of exposure required for the canisters and also to quantify the extent of interaction between the canister and the bentonite buffer system. Because of practical reasons, all the tests have been and must be carried out over a considerably shorter time than the required lifetime of the disposal canisters.

Based on thermodynamics, highly saline groundwater has been predicted to subject the canister material, pure copper, to general corrosion under quasi-anoxic conditions [1, 2]. When bentonite is present it is suspected to act as a diffusion barrier and to slow down the corrosion rate of copper markedly.

This work concerns the effect of bentonite in contact with groundwater on the corrosion of copper in a closely simulated final disposal vault environment of radioactive waste.

## 2 Goal

The goal of this work is to perform long term corrosion monitoring tests of Cu in simulated final nuclear waste repository in the presence of wetted bentonite. In order to effectively verify the extent of simulation of the redox conditions and to obtain

a reliable estimate the corrosion rate two sensors have to be evaluated, a reference electrode that has a long enough lifetime in the presence of bentonite and an on-line corrosion rate sensor.



## 3 Description of the target

The target of the present work is to develop and test the following sensors:

### 3.1 A modified reference electrode

The existing external pressure balanced AgCl/Ag reference electrode design will be modified to allow potential measurements in the presence of highly hydrophilic compacted bentonite. To this end, it will be filled with bentonite slurry prepared by wetting MX80 bentonite in highly saline groundwater.

### 3.2 Corrosion rate sensor

A resistance probe for on-line corrosion rate monitoring will be constructed to allow the use of pure copper as the sensor material and to allow for reliable functioning in the presence of compacted bentonite. The probe consists of a thin wire through which a constant current is led. The signal is the measured voltage, from which the resistance and the corresponding reduction in the wire diameter will be calculated.

## 4 Experimental methods

In this project the electrode designs for the measurement of redox-potential and corrosion rate of copper are evaluated in highly saline groundwater in the presence of compacted MX80 bentonite. The electrode designs are discussed in more detail in Appendix. The experiments are performed in highly saline groundwater (HSGW) with chloride content that is roughly 53800 mg/l (1.52 M) in a static Ti-cladded autoclave at a temperature of 80 °C and pressure of 14 MPa. 5N Nitrogen gas further purified using an Oxisorb gas purification system is used to remove oxygen from the solution. Phosphorus deoxidised copper (Cu-OFP) is used as test material for the weight loss coupons. The resistance wire probe was manufactured from copper wire with a diameter of 0.125 mm acquired from Goodfellow Ltd. The compositions of the materials are shown in Table I. The modified AgCl/Ag electrode filled with wetted bentonite and the Cu-resistance probe corrosion rate sensor are im-

mersed in the wetted bentonite. The exact compaction level of the bentonite in these sensors is not, however, exactly known. A Pt flag electrode is immersed in the reference groundwater above the bentonite slurry. A separate stainless steel vessel filled with wetted bentonite and comprising a Cu disc electrode insulated with epoxy resin, a Pt counter electrode and a AgCl coated Ag wire acting as a reference electrode is mounted in the autoclave. The bentonite becomes compacted to some extent when the stainless steel vessel is closed. However, the exact compaction level cannot be determined in this kind of system. The separate stainless steel vessel is used as an inserted electrochemical cell for the impedance measurements and the two standard corrosion coupon specimens. All the autoclave system has been maintained at the temperature of 80 °C and a pressure of 14 MPa for ca. 170 h.

**Table I.** Composition (in ppm) of the test materials.

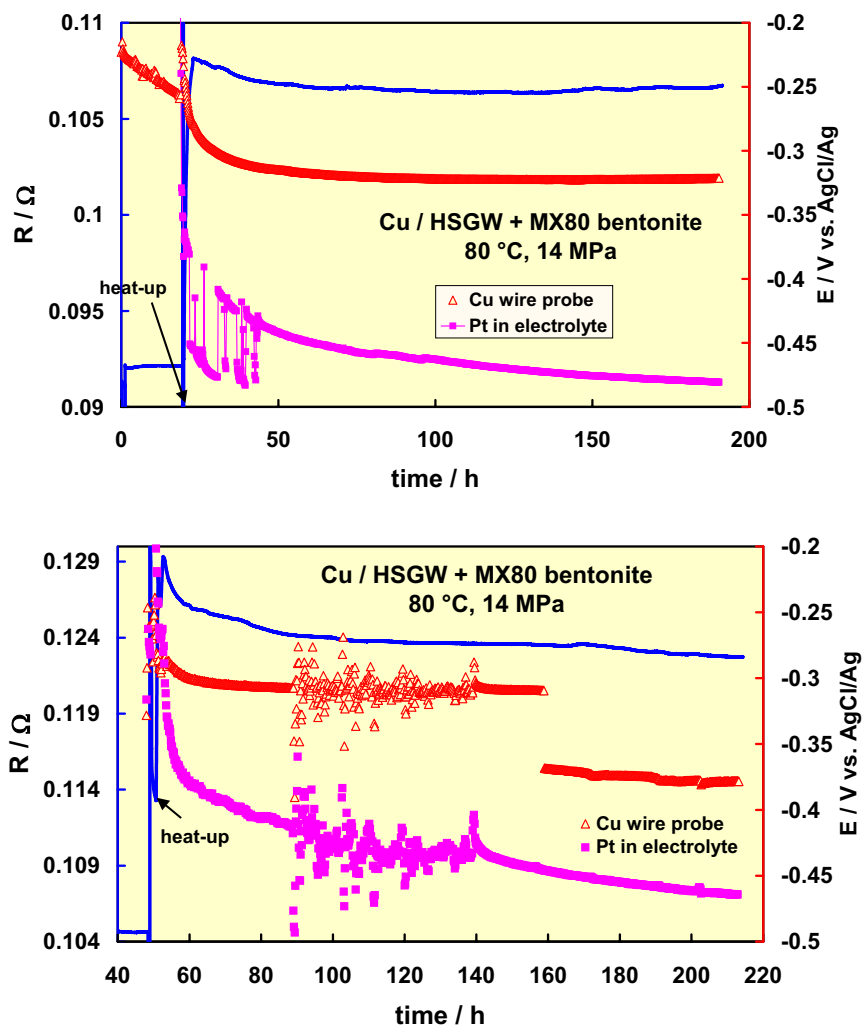
	Ag	Al	Bi	Ca	Fe	Mg	Mn	Na	Pb	Si	P	O
<b>Cu99.99% Goodfellow</b>	7	1	<1	<1	1	<1	<1	<1	<1	2	NA	NA
<b>Cu-OFP</b>	NA	NA	NA	NA	2	NA	NA	NA	NA	NA	45	1.5

## 5 Results and discussion

### 5.1 Resistance of the Cu probe, corrosion and redox potentials

Fig. 1 shows the evolution of the resistance of the Cu corrosion probe, the potential of the Cu corrosion probe and the potential of the Pt electrode in the free electrolyte above the bentonite slurry during the two tests performed. The potentials of Cu and Pt were measured against the modified

AgCl/Ag electrode filled with wetted bentonite. The disturbances between the 90th and 140th hour of the experiment in the second test (Fig. 1) are due to the external disturbances in electrical network caused most probably by some other measurement device. Fig. 2 represents a magnification of the region following immediately the heat-up of the autoclave to 80 °C (at ca. 19.5h in



**Fig. 1.** The evolution of the resistance of the Cu corrosion probe sensor (solid line, left axis), the potential of the Cu corrosion probe sensor and the potential of the Pt in the groundwater with time during the first test (above) and the second test (below). The potentials are measured vs. the modified AgCl/Ag electrode filled with wetted bentonite.

the first test and ca. 49 h in the second test).

Regarding the operation of the sensors developed in the present project, the following observations can be made:

- The resistance of the Cu corrosion probe starts to increase immediately after heat-up, indicating copper corrosion. The extent of corrosion as monitored by the resistance change follows a power law similar to parabolic and practically levels off after ca. 4 h after the heat-up. A small decrease in the resistance is observed after that, possibly due to redeposition of Cu in a reverse reaction. The resistance signal stays stable after that for at least 150 h in two successive tests. These results indicate that the Cu corrosion probe can be regarded as a reliable

sensor to monitor the corrosion rate in wetted bentonite.

- The potentials of both the Cu probe in wetted bentonite and the Pt probe in the free electrolyte measured vs. the modified reference electrode filled with wetted bentonite exhibit a slowly decreasing trend during the whole duration of the experiments. The potential of the Pt in the free electrolyte reaches after 150 h a value of  $-0.48$  V vs. modified AgCl/Ag, which can be estimated to be close to  $-0.31$  V<sub>SHE</sub>. This value indicates quasi-anoxic conditions in the groundwater, according to the expectations after purging with nitrogen gas purified with Oxisorb system. The potential of the Cu probe stabilises at  $-0.32$  V vs. modified AgCl/Ag, i.e.

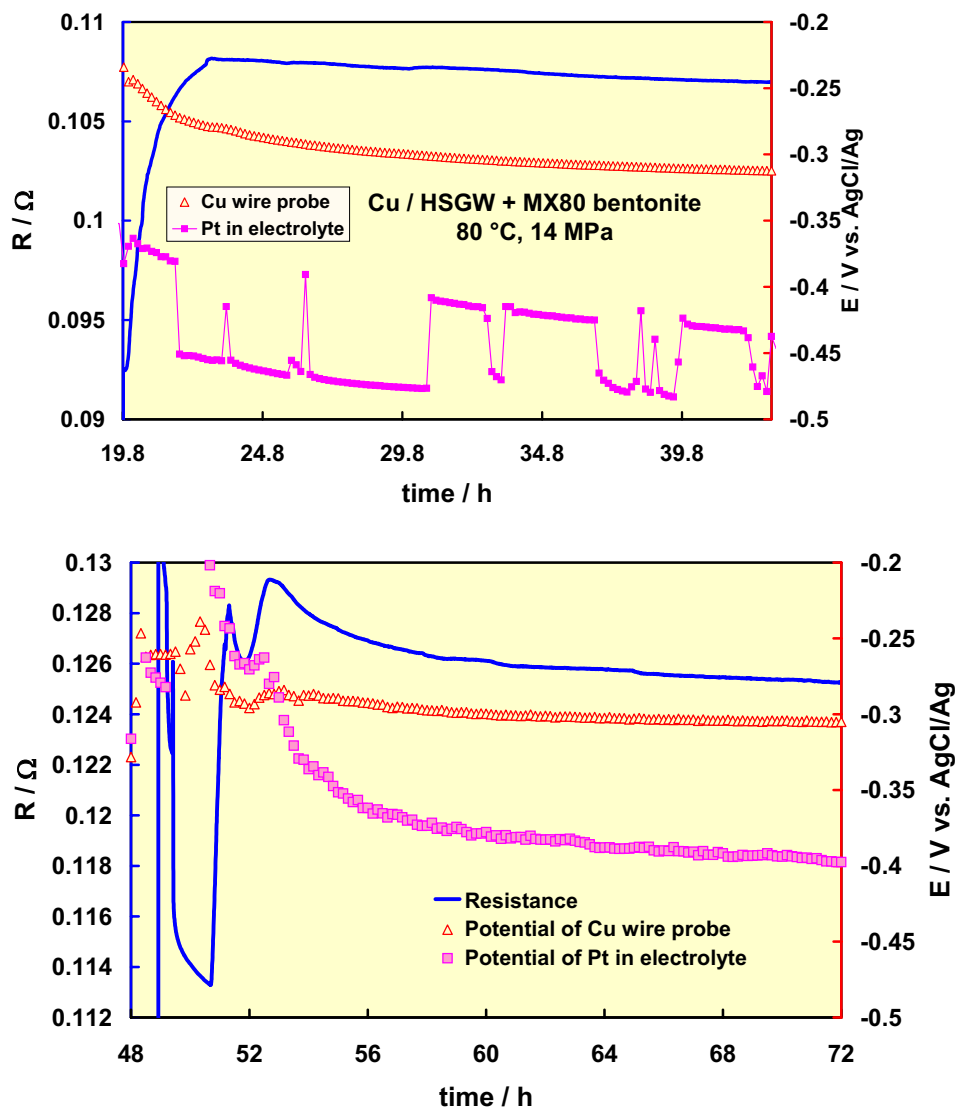


Fig. 2. The evolution of the resistance of the Cu corrosion probe sensor (solid line, left axis), the potential of the Cu corrosion probe sensor and the potential of the Pt in the groundwater with time during the first test (above) and the second test (below). Magnification of the first day after heat-up.

around  $-0.15 V_{SHE}$ , which is in accordance to earlier tests in simulated groundwater without bentonite [1, 2]. All this observations show that the developed modified reference electrode can be regarded as a reliable tool to measure the potentials in wetted bentonite at least for 150 h.

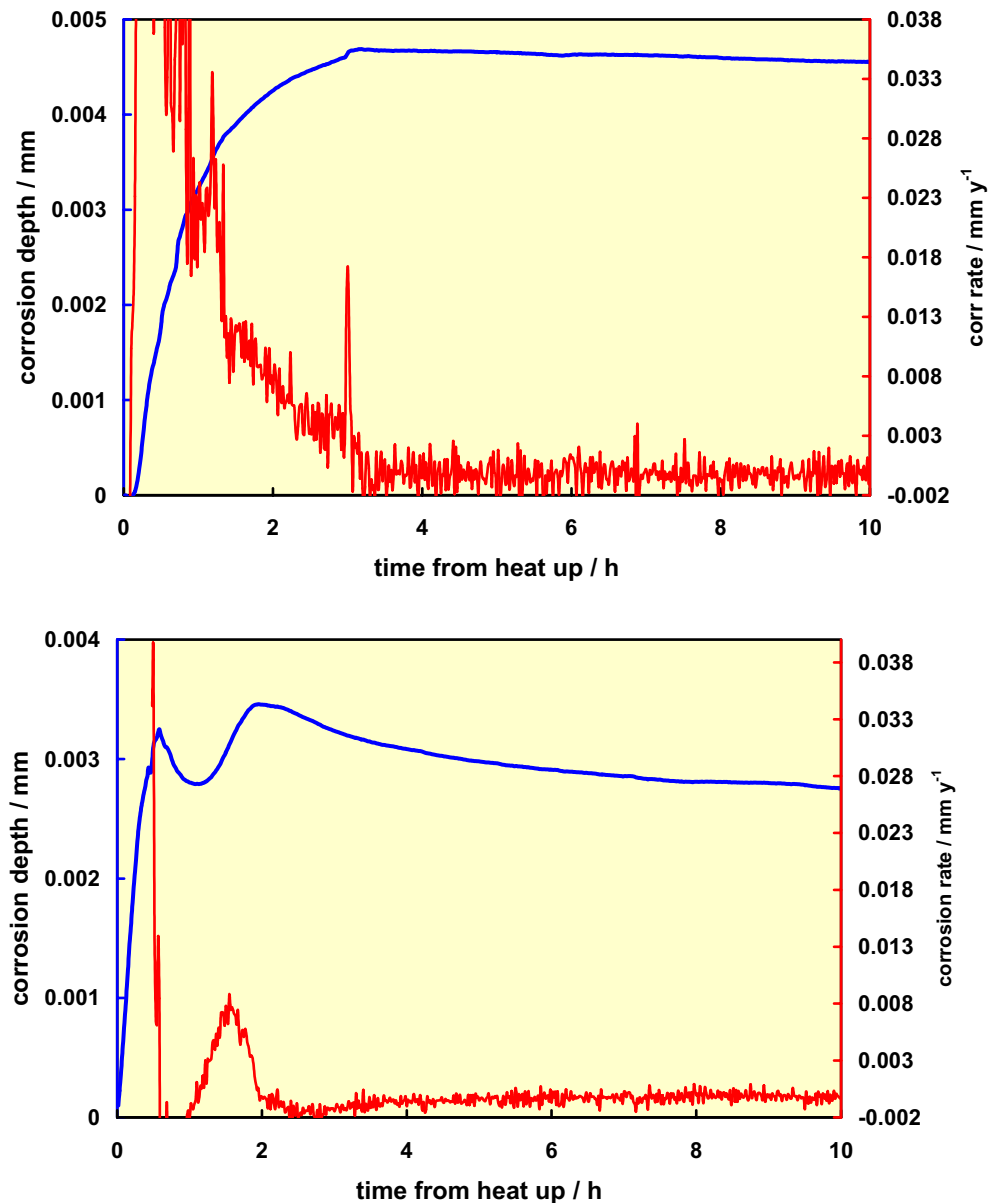
The depth of corrosion penetration,  $d_{corr}$ , can be estimated from the resistance according to the following formula [3]

$$d_{corr} = r_0 \left( 1 - \sqrt{\frac{R_0}{R}} \right)$$

where  $r_0$  and  $R_0$  are the initial values of the radius and the resistance of the probe,  $R$  is the resistance during corrosion. Differentiating this formula with respect to time gives us the possibility to estimate the corrosion rate (depth penetration rate) as

$$\Delta_{corr} = 0.5r_0 \sqrt{\frac{R_0}{R}} \frac{1}{R} \frac{dR}{dt}$$

Fig. 3 shows the values of  $d_{corr}$  and  $D_{corr}$  for the first 10 h after heat up in the two experimental runs presented. The agreement between the two figures is relatively good, indicating the good reproducibility of the measurements of corrosion



**Fig. 3.** Corrosion depth (mm) and instantaneous corrosion rate (in  $\text{mm y}^{-1}$ ) calculated from the resistance probe data shown in Figs 1–2.

rates with the sensor based on the resistance probe. Further, it can be argued that an appreciable depth penetration of the corrosion process occurs only in the first 4–5 hours of the experiment, likely to be associated with the consumption of the residual oxygen in the autoclave. The corrosion rate in the subsequent period becomes undetectable with the sensor and thus below  $0.5 \mu\text{m y}^{-1}$ . The results shown in Fig.3 indicate even a decrease of the penetration depth with time possibly because of a redeposition of dissolved Cu on the resistance probe.

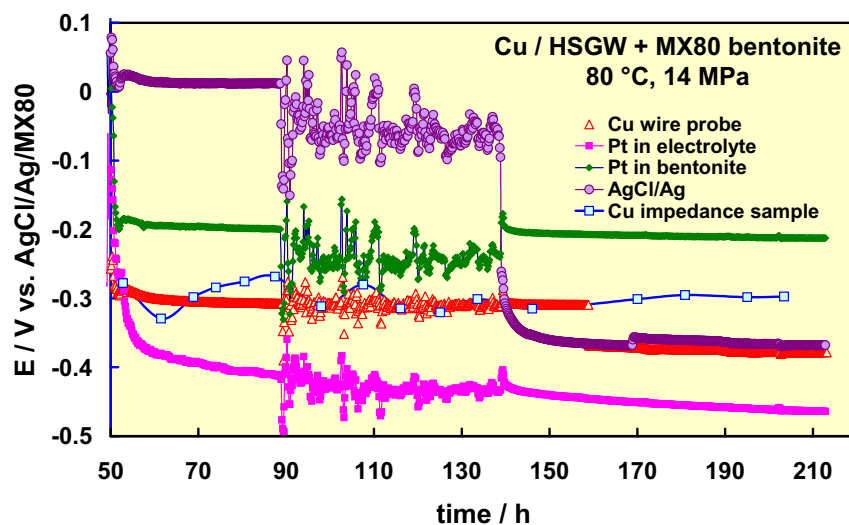
Fig. 4 shows a comparison of the potentials for the Cu resistance probe, Cu in the small vessel filled with bentonite, Pt in the electrolyte, Pt in the small vessel filled with bentonite and the AgCl covered Ag wire in the small vessel filled with bentonite during the second test. All the potentials are expressed vs. the modified AgCl/Ag reference electrode filled with bentonite. It is important to note that external electrical disturbances have been experienced by the measurement system between the 90th and 140th hour of the experiment duration.

The following tentative conclusions regarding the comparison of the redox conditions in the free HSGW and in the bentonite slurry can be made:

- The corrosion potentials of the Cu resistance probe and the Cu in the small vessel filled with bentonite are close to each other assuming an

average value of ca.  $-0.3 \text{ V}$  vs. the AgCl/Ag electrode filled with bentonite, i.e. around  $-0.13 \text{ V}$  vs. SHE in accordance with earlier measurements in plain HSGW [1, 2, 4]. On the other hand, the potential of the Pt electrode in the small vessel filled with bentonite is ca.  $0.18 \text{ V}$  more positive than that of the Pt electrode in the free HSGW (Fig. 3). Thus it can be stated that the corrosion potential of Cu is not influenced by the fact that the redox conditions in and out of the bentonite are significantly different. A tentative conclusion is that the corrosion potential of Cu in the quasi-anoxic conditions reached in the present study is determined by copper containing redox systems in the vicinity of the copper surface.

- The potential of the AgCl covered Ag wire immersed in the small bentonite vessel is relatively stable and its potential is close to that of the modified AgCl/Ag electrode filled with bentonite only up to 90 h (Fig. 3). After the electrical disturbances, the potential of this electrode is ca.  $0.35 \text{ V}$  more negative than that of the modified AgCl/Ag electrode. After the test a visual examination revealed that the AgCl coating had largely dissolved. It is thus not advisable to use such a reference electrode for prolonged corrosion tests in HSGW-wetted bentonite.



**Fig. 4.** Summary of the potentials of the Cu resistance probe, Pt in electrolyte, Pt in bentonite, the separate Cu electrode during impedance measurements and the AgCl covered Ag wire in bentonite during the second test. External electrical disturbances have been experienced between 90 and 140 h.

## 5.2 Impedance spectroscopic results

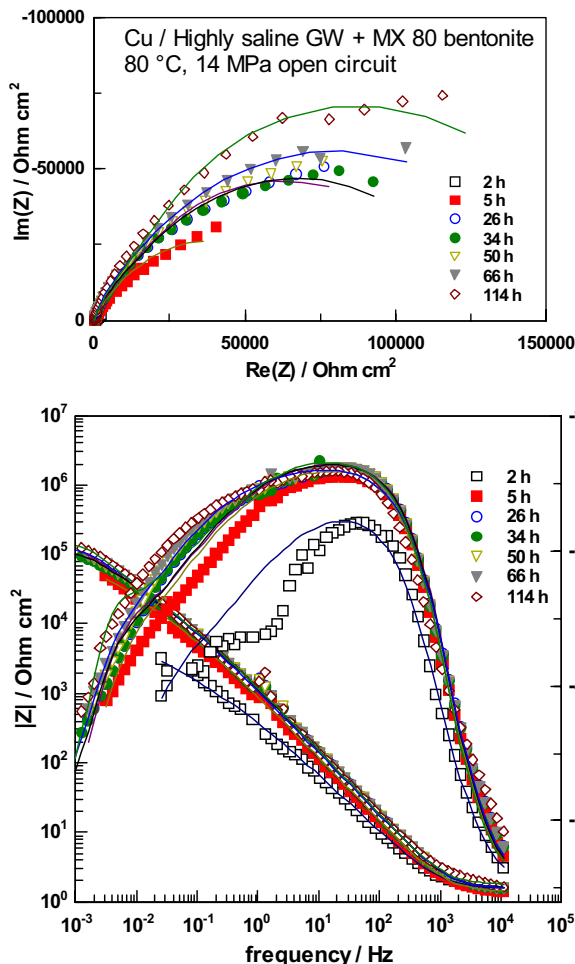
Figs 5 and 6 show the evolution of the impedance spectra of a separate Cu disc electrode measured during the first and second tests in the inserted vessel filled with wetted bentonite. The AgCl-coated silver wire was used as a reference and a Pt wire as a counter electrode, both immersed in the wetted bentonite.

The impedance magnitude at low frequencies increases significantly in the first 26 h of the first test (Fig.5), which is followed by a much slower increase and a stabilisation at ca. 90 h. The phase angle curve of the impedance spectra is broadly analogous to what has been measured earlier in groundwater without bentonite [1, 4].

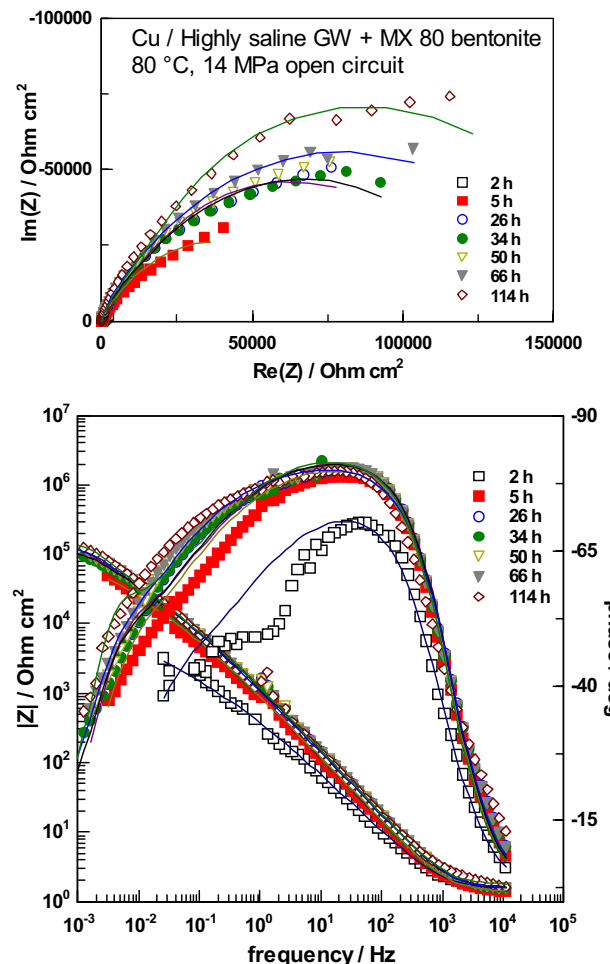
However, in the second test the impedance magnitude at low frequencies is several times

smaller than that in the first test (Fig. 6). The impedance magnitude seems to decrease with time up to ca. 90 h, and then starts to increase again. This behaviour is to a certain extent correlated to the electrical disturbances experienced by the system which started at ca. 90 h and resulted in a dramatic change of the potential of the AgCl covered Ag wire used as a reference electrode in the impedance measurements. Thus the second set of impedance measurements is to be regarded as less reliable than the first. This demonstrates once more that impedance spectroscopy and other electrochemical techniques have to be used with caution to monitor the corrosion of copper in nuclear waste repository conditions, as already discussed earlier by us [4].

The impedance data were fitted to the transfer



**Fig. 5.** Evolution of the impedance spectra of copper in the bentonite wetted with highly saline groundwater with time during the first test. (above) complex plane plot, (below) Bode plot. Points: experimental data; lines: best-fit calculation according to the model described in [4].



**Fig. 6.** Evolution of the impedance spectra of copper in the bentonite wetted with highly saline groundwater with time during the second test: (above) complex plane plot, (below) Bode plot. Points: experimental data; lines: best-fit calculation according to the model described in [4].



function proposed earlier for the corrosion of Cu in HSGW in the absence of bentonite [4]. The polarisation resistance calculated from this procedure from the data pertinent to the first and second tests is shown in Figs. 7 and 8 (left axis). Obviously, it follows the trend of the impedance magnitude at low frequencies (cf. Figs 5–6).

The corrosion current density is evaluated from the polarisation resistance,  $R_p$ , as follows:  $i_{\text{corr}} = B / R_p$ , where  $B$  is the Stern-Geary coefficient (a conservative value of this coefficient can be  $B=0.0065$  V according to Ref. [4]). From the corrosion current density, the corrosion rate in terms of penetration depth can be estimated:  $D = 3.154 \cdot 10^8 i_{\text{corr}} A_{\text{Cu}} / (r_{\text{Cu}} F)$ , where  $A_{\text{Cu}}$  is the atomic mass of Cu ( $63.55 \text{ g at}^{-1}$ ),  $\rho_{\text{Cu}}$  is its density ( $8.94 \text{ g cm}^{-3}$ ) and  $F$  is the Faraday constant ( $96487 \text{ C mol}^{-1}$ ). The time evolution of the corrosion penetration rate is also plotted in Figs 7 and 8 (right axis).

The corrosion rate estimated from the impedance measurements in the first test decreases with time of exposure and reaches a saturation value of ca.  $0.9 \text{ mm y}^{-1}$ . This rate is more than an order of magnitude lower than that estimated from impedance measurements in saline groundwaters in the absence of bentonite [1, 2, 4]. However, the value estimated from the data measured at the end of the second test is ca.  $4 \text{ mm y}^{-1}$ , which is already comparable with, albeit still lower than, the data in HSGW in the absence of bentonite.

Summarising, impedance spectroscopic measurements indicate that the mechanism of the anodic process during corrosion of copper in saline

groundwater is probably unchanged in the presence of wetted bentonite. The estimated corrosion rate from impedance measurements, which is likely to be associated with the rate of the anodic process, is somewhat lower in the presence of bentonite. However, also in the present work the results from the impedance measurements are associated with large uncertainty.

### 5.3 Weight loss coupon results

Two weight loss samples were exposed to the groundwater in bentonite in both conducted tests. The weight loss of the specimens was  $0.7 \text{ mg}$  in the first test and  $0.8 \text{ mg}$  in the second test. The general corrosion rate was calculated using the formula

$$\Delta = \frac{\Delta m \cdot 3650}{\rho \cdot A \cdot t} [\text{mm} / \text{y}]$$

where  $\Delta m$  = weight loss [g],  $\rho$  = density [ $\text{g cm}^{-3}$ ],  $A$  = surface area [ $\text{cm}^2$ ] and  $t$  = exposure time [days]. The density of copper is  $8.94 \text{ g cm}^{-3}$ . The calculated corrosion rate is  $0.0029 \text{ mm y}^{-1}$ , i.e.  $2.9 \text{ mm y}^{-1}$ . This corrosion rate reflects the rather high initial corrosion rate, which was also estimated from the impedance spectroscopic results. The corrosion rate is clearly higher than the acceptable average corrosion rate,  $0.5 \text{ mm y}^{-1}$ . However, this result can be interpreted in connection to Fig. 3 by assuming that the measured weight loss reflects only the instantaneous corrosion rate in the initial oxidic period.

Figs. 9 to 12 show the surface appearance of

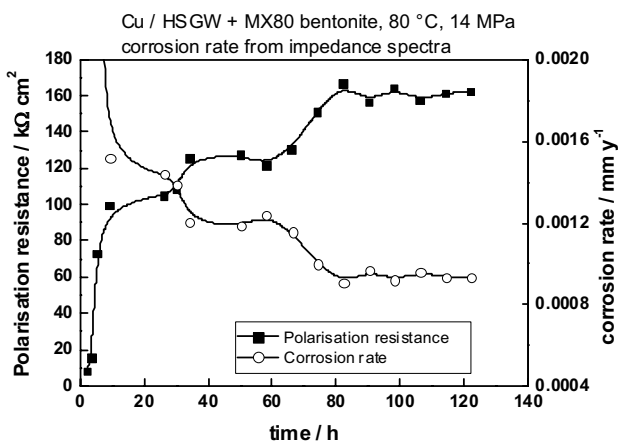


Fig. 7. Polarisation resistance (left) and corrosion rate as penetration depth over time (right) evaluated by analysis of the impedance spectra as depending on time during the first test.

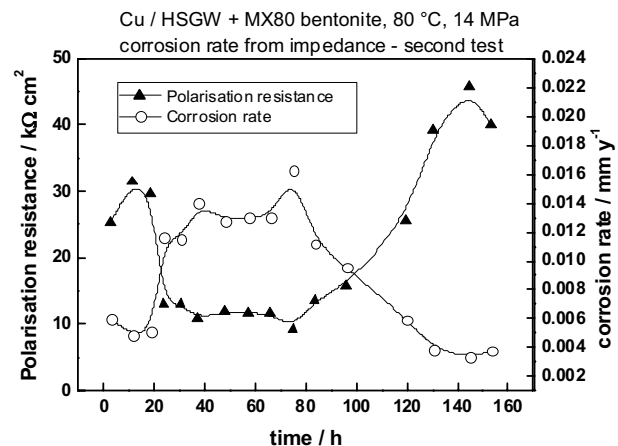
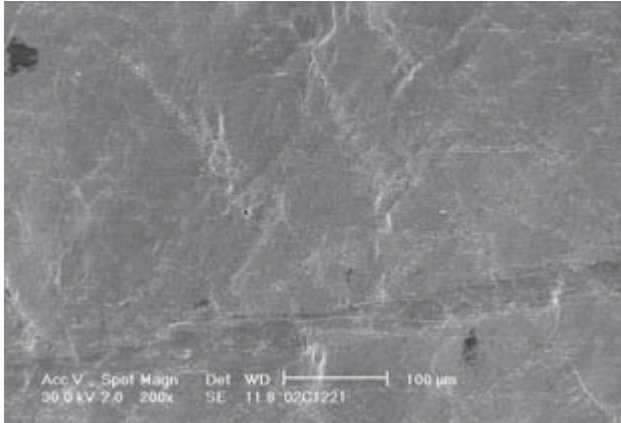


Fig. 8. Polarisation resistance (left) and corrosion as penetration depth over time (right) evaluated by analysis of the impedance spectra as depending on time during the second test.

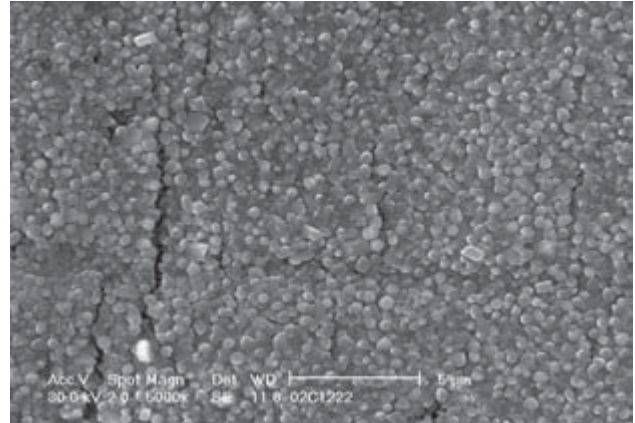


the weight loss coupons. The surfaces were generally smooth (Fig. 9), showing a surface morphology indicating presence of a crystalline surface film, Fig. 10. In earlier test runs without the

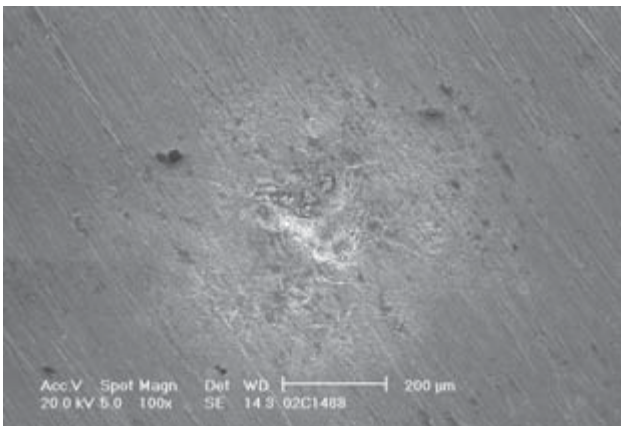
presence of bentonite the surface has been smooth and free of crystalline film [2]. In this test one pit-like formation was detected, Figs 11 and 12. The width of the pit-like formation was about 0.1 mm.



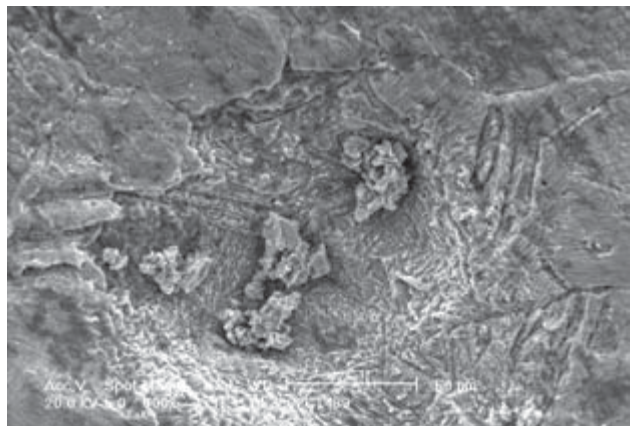
**Fig. 9.** Surface of the corrosion coupon, general appearance.



**Fig. 10.** Surface of the corrosion coupon, detailed appearance.



**Fig. 11.** Surface of the corrosion coupon, pit-like formation.



**Fig. 12.** Surface of the corrosion coupon, detail of the pit-like formation.

## 6 Conclusions

The following conclusions regarding the viability of the sensors developed as a result of this work can be drawn:

- The resistance of the corrosion probe reacts to copper corrosion immediately after immersion. The corrosion process detectable by the probe practically stops after ca. 4 h after the heat-up. A small decrease in the resistance is observed after that, possibly due to redeposition of Cu. The resistance signal was followed up to at least 150 h in two successive test runs. These results indicate that the Cu corrosion probe can be regarded as a reliable sensor to monitor the corrosion rate in wetted bentonite.
- The potential of platinum in the electrolyte measured vs. the modified reference electrode filled with wetted bentonite showed a slowly decreasing trend during the whole duration of the experiments and reached after 150 h a value close to  $-0.31 V_{SHE}$ . This value indicates quasi-anoxic conditions in the groundwater, according to the expectations after purging with nitrogen gas purified with Oxisorb system. Simultaneously, the potential of copper stabilises around  $-0.15 V_{SHE}$ , in accordance with earlier tests in simulated groundwater without bentonite. These observations show that the developed modified reference electrode can be regarded as a reliable tool to measure the potentials in wetted bentonite.
- The AgCl coated Ag wire, used as an internal reference electrode was embedded in bentonite saturated with ground water and exposed to 80 °C and 14 MPa. This electrode design was found to be unstable.

## 7 Summary

In the present work, the feasibility of two sensors—an on-line corrosion rate monitoring sensor and a modified reference electrode—has been tested with respect to Cu corrosion in highly saline groundwater filled with MX80 bentonite in conditions closely simulating those in a nuclear waste repository. As a result, it can be stated that both sensors showed the expected stability at least up to 150 h of operation. Thus it is expected that they can be used for reliable long-term corrosion rate and electrode potential measurements in the presence of wetted bentonite. In addition, it has been demonstrated that after an initial transient peri-

od of ca. 5–8 h, Cu corrosion in highly saline groundwater filled with MX80 bentonite becomes undetectably low because of the anoxic conditions reached in the free groundwater. At the same time, the corrosion potential of Cu is still in the active corrosion region according to thermodynamic calculations. Furthermore, redox potentials in the bentonite slurry remain significantly higher than in the free groundwater. This means that the decomposition of the oxygen contained in the gas-filled pores of the bentonite is a process occurring in a time scale larger than that of the present experiments.

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## Appendix Electrode designs

### 1. Resistance wire

The resistance wire electrode design is shown in Fig. A-1. The length of the electrode is 225.5 mm and the internal diameter is 10 mm. The electrode body and the parts are made of zirconium metal and oxidised in air oven to grow an electrically insulating oxide layer on the surface. The resistance wire of Cu is placed inside the tubular body which is then filled with bentonite which has been saturated with saline ground water. The end of the electrode is covered with a porous ceramic plug providing an electrolyte bridge from the resistance wire to the free groundwater surrounding the probe head. The ceramic plug is pressed to the bentonite and fixed using a metal plunge with holes in it for free flow of water. The electrical wires from the resistance wire are brought across

the pressure boundary from the other end of the electrode through box type sealing applying graphite seals.

### 2. Reference electrode

The reference electrode design is simply the conventional external pressure balanced reference electrode (EPBRE) with AgCl/Ag sensor head. In this design the sensor head is situated at the room temperature end of the sensor and is thus under stable conditions. The electrolyte bridge (PTFE-tube) is filled with bentonite saturated with saline ground water. The signal wire is brought across the pressure boundary from the room temperature end of the electrode through box type sealing applying a graphite seal.

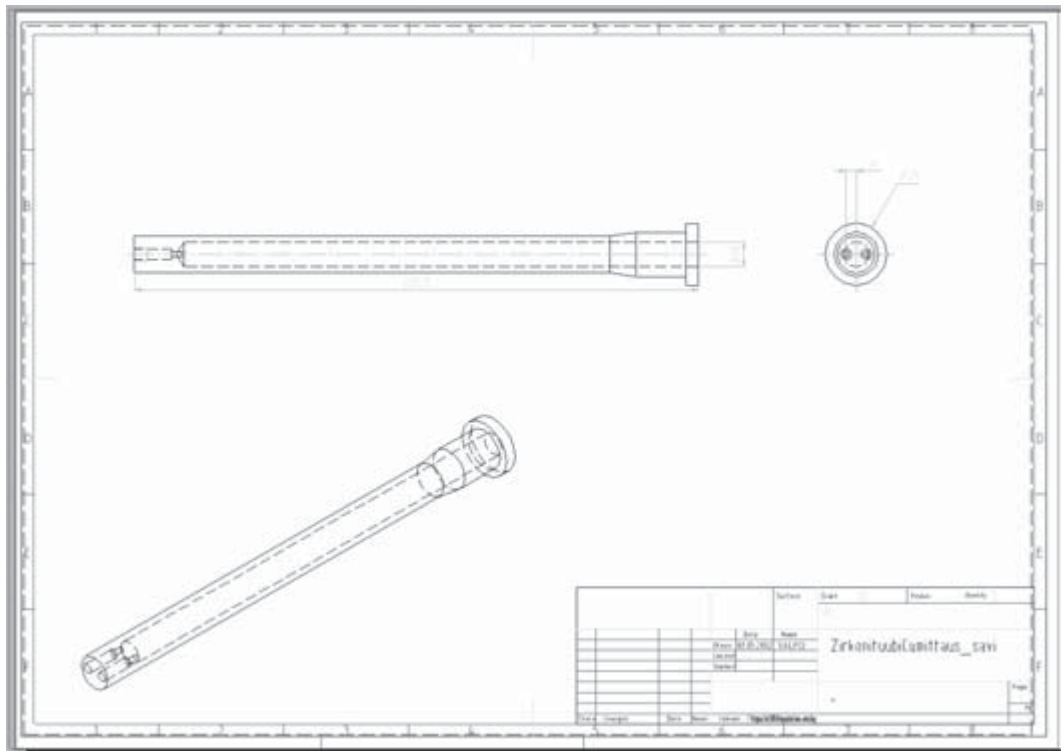


Fig. A-1. The resistance wire probe design.