

Application of an On-line Corrosion Probe and a Reference Electrode for Copper Corrosion Studies in Repository Conditions

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ABSTRACT

Two sensors, an on-line corrosion sensor based on the wire-resistance probe design and a reference electrode which are applicable in repository conditions are introduced. Both sensors have been tested in simulated repository conditions in bentonite saturated with highly saline groundwater at 80 °C temperature and 14 MPa pressure up to 150 h exposure. In addition, it has been demonstrated that after an initial transient period of ca. 5-8 h, Cu corrosion in highly saline groundwater filled with bentonite becomes undetectably low probably because of the anoxic conditions reached in the free groundwater. At the same time, the measured corrosion potential of Cu is still in the active corrosion region. Furthermore, redox potentials in the wetted bentonite remain significantly higher than in the free groundwater. This may mean that the decomposition of oxygen contained in the pores of the bentonite is a process occurring in a time scale larger than that of the present experiments.

INTRODUCTION

The Scandinavian concepts suggested until now to dispose of high-level radioactive wastes adopt a near-field multibarrier engineering system, consisting of the form of the waste itself, a containment of the waste form (i.e. a metal canister) and a bentonite buffer which will surround and isolate the canister from the host bedrock. The canisters are designed to resist corrosion, pressure, 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.

In Finland at the selected site of Olkiluoto and in Sweden at the candidate sites the groundwater has been found to contain appreciable amounts of chlorides. 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 suggested to act as a diffusion barrier and to slow down the corrosion rate of copper markedly. The present work addresses the effect of bentonite in contact with groundwater on the corrosion of copper in a closely simulated final disposal vault environment. The longer-term goal of this project is to perform corrosion monitoring tests of Cu in simulated final nuclear waste repository in the presence of wetted bentonite for extended time periods. In order to effectively verify the extent of simulation of the redox conditions and to obtain a reliable estimate of 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.

EXPERIMENTAL DETAILS

The experiments have been carried out for 170 h in highly saline groundwater (HSGW) containing 53800 mg/l (1.52 M) of chloride in a Ti-clad autoclave at 80 °C and a pressure of 14 MPa. 99.999% N₂ gas further purified using an Oxisorb oxygen scavenger system (<5 ppb O₂ in the autoclave inlet gas) was used to remove oxygen from the solution. Oxygen-free phosphorous microalloyed copper (Cu OFP, 45 ppm P and 1.5 ppm O) was employed as material for the weight loss coupons. The wire resistance probe was made of Cu (99.95%, Goodfellow, diameter 0.125 mm, length 45 mm). A modified AgCl/Ag electrode filled with MX-80 bentonite wetted by the HSGW and the Cu-wire probe were immersed in the wetted MX-80 bentonite. A dc current of 85 mA was fed through the Cu probe and the resulting voltage drop was continuously recorded to monitor the wire probe resistance. A Pt electrode was immersed in the reference groundwater above the MX-80 bentonite slurry. A separate stainless steel vessel filled with wetted MX-80 bentonite, comprising a Cu disc electrode insulated with epoxy resin, a Pt counter electrode and a AgCl coated Ag wire reference electrode, was mounted in the autoclave. The separate vessel was used as an inserted electrochemical cell for impedance measurements and the weight loss coupons. Impedance measurements were carried out at the free corrosion potential with a PAR 283 / 5210 system controlled by Power Suite software (Perkin Elmer).

RESULTS AND DISCUSSION

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. The potentials of Cu and Pt were measured against the modified AgCl/Ag electrode filled with wetted bentonite.

The resistance of the Cu-wire 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 (cf. Fig. 1b). 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_{SHE}. 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. around -0.15 V_{SHE}, which is in accordance to earlier tests in simulated groundwater without bentonite [1,2]. All these observations indicate 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.

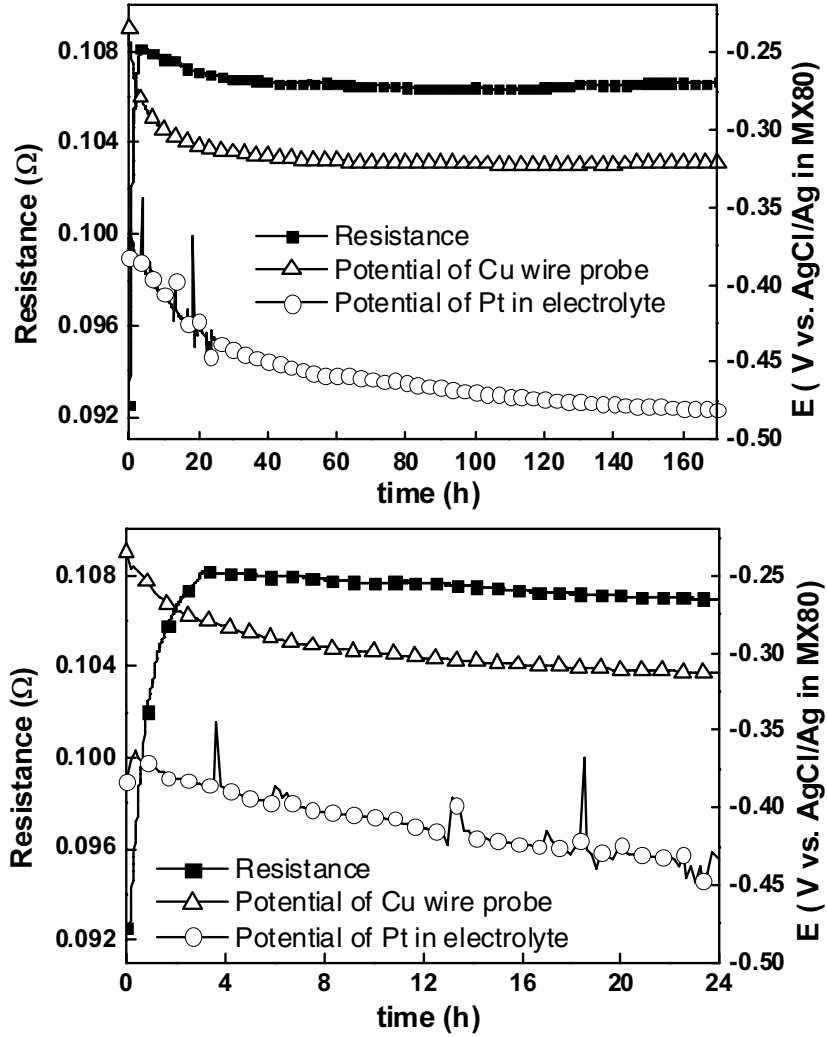


Figure 1. (above) The evolution of the resistance of the Cu corrosion probe sensor (filled squares, left axis), the potential of the Cu corrosion probe sensor and the potential of the Pt in the groundwater. The potentials are measured vs. the modified AgCl/Ag electrode filled with wetted bentonite; (below) magnification of the first day of exposure at 80 °C, 14 MPa.

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

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

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 d_{corr} with respect to time gives the possibility to estimate the corrosion rate Δ_{corr} .

Fig. 2 shows the values of d_{corr} and Δ_{corr} for the first 12 h of exposure. 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.2 indicate even a decrease of the penetration depth with

time possibly because of a redeposition of dissolved Cu on the resistance probe. An average corrosion rate of $2.9 \mu\text{m y}^{-1}$ was calculated from the weight loss measurements, probably reflecting the high initial corrosion rate (Fig.2). The corrosion rate is clearly higher than the acceptable average corrosion rate, $0.5 \mu\text{m y}^{-1}$. However, this result can be interpreted in connection to Fig. 2 by assuming that the measured weight loss reflects only the transient corrosion rate in the initial oxic period.

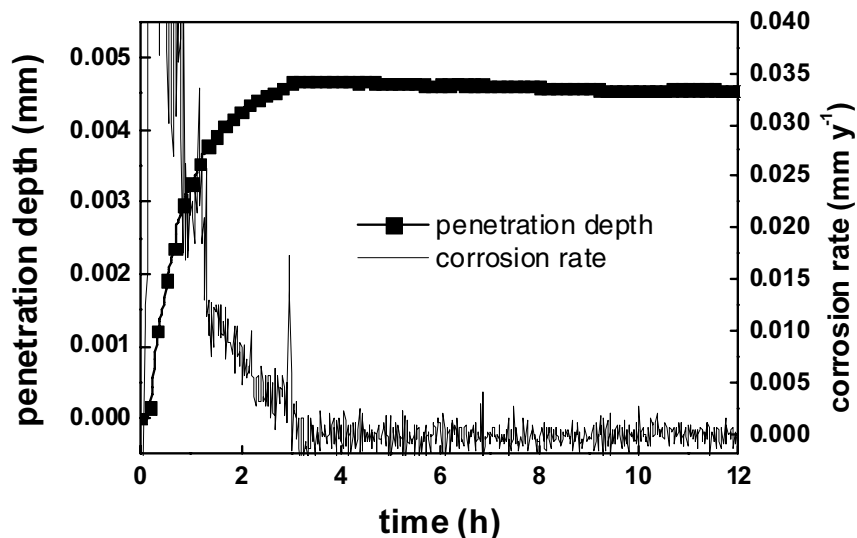


Figure 2. Penetration depth of corrosion (mm) and instantaneous corrosion rate (in mm y^{-1}) calculated from the resistance probe data shown in Fig. 1.

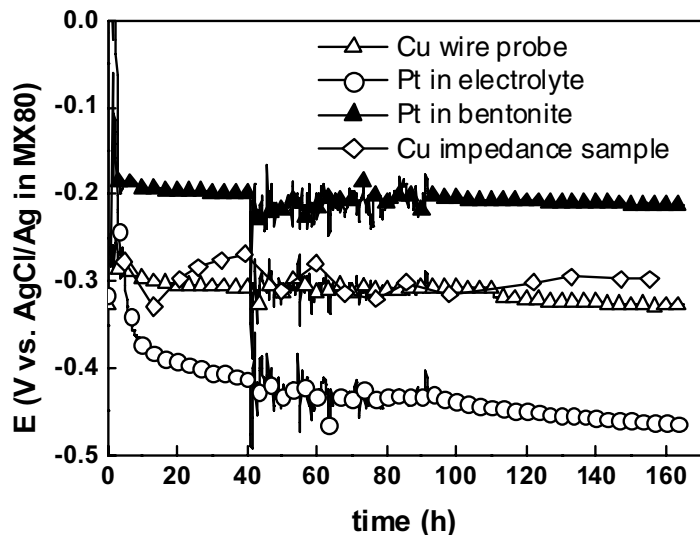


Figure 3. Summary of the potentials of the Cu resistance probe, Pt in electrolyte, Pt in bentonite, and Cu electrode in bentonite (impedance sample) during exposure.

Figure 3 shows a comparison of the potentials of the Cu resistance probe, Cu in the small vessel filled with bentonite (impedance sample), Pt in the electrolyte, Pt in the small vessel filled with bentonite during exposure. All the potentials are expressed vs. the modified AgCl/Ag reference electrode filled with bentonite. The corrosion potentials of the Cu resistance probe and

the Cu in the small vessel filled with bentonite are close to each other with an average value of ca. -0.3 V vs. the AgCl/Ag electrode filled with bentonite, i.e. around -0.13 V_{SHE} in accordance with earlier measurements in bentonite-free 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 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 inside and outside 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.

Impedance spectroscopic measurements

Fig. 4 shows the evolution of the impedance spectra of the Cu disc electrode measured in the inserted vessel filled with wetted bentonite. A AgCl-coated silver wire was used as a reference and a Pt wire as a counter electrode, both immersed in the wetted bentonite.

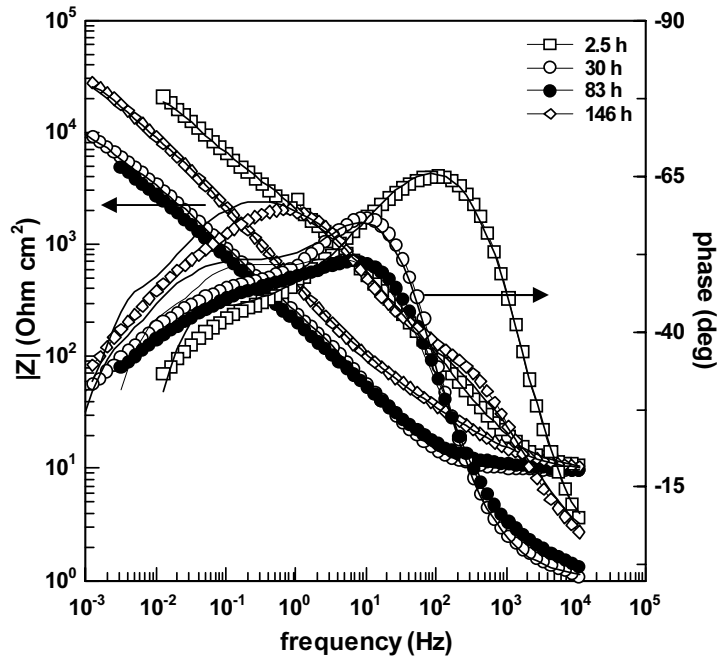


Figure 4. Evolution of the impedance spectra of copper in the bentonite wetted with highly saline groundwater with exposure. Points - experimental data, lines - best-fit calculation according to the model described in [4].

The impedance magnitude at low frequencies seems to decrease with time up to ca. 90 h, and then starts to increase again. The phase angle curves of the impedance spectra are broadly analogous to what has been measured earlier in groundwater without bentonite [1,4]. The impedance data were fitted to the transfer function proposed earlier for the corrosion of Cu in HSGW in the absence of bentonite [4]. The corrosion rate was estimated from the polarisation resistance, R_p , as follows [4,5]:

$$\Delta_{\text{corr}} = 3.154 \cdot 10^8 \text{ B A}_{\text{Cu}} / (R_p \rho_{\text{Cu}} F)$$

where B is the Stern-Geary coefficient related to the polarisabilities of the anodic and cathodic reactions, (a conservative value of 0.0065 V was adopted according to Refs. 4,5), A_{Cu} is the atomic mass of Cu (63.55 g at⁻¹), ρ_{Cu} is the density of Cu (8.94 g cm⁻³) and F is the Faraday constant (96487 C mol⁻¹). The value estimated from the impedance data at the end of exposure is ca. 4 $\mu\text{m y}^{-1}$, which is lower but comparable with the data in bentonite-free HSGW [4].

Summarising, impedance measurements indicate that the mechanism of the anodic process 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 [4], 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.

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 exposure at 80 °C. A small decrease in the resistance is observed after that, possibly due to the redeposition of Cu. 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 Pt in the electrolyte measured vs. the modified reference electrode showed a slowly decreasing trend during the whole duration of the experiments and reached ca. -0.31 V_{SHE} after 150 h. This value indicates quasi-anoxic conditions in the groundwater. Simultaneously, the potential of copper stabilises around -0.15 V_{SHE}, in accordance with earlier tests in simulated groundwater without bentonite. These observations demonstrate the reliability of the developed reference electrode. The potential values suggest that the decomposition of 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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REFERENCES

1. T. Laitinen, K. Mäkelä, T. Saario, and M. Bojinov, SKI Report 01:2, Swedish Nuclear Power Inspectorate, Stockholm, 2001.
2. T. Saario, K. Mäkelä, T. Laitinen, and M. Bojinov, STUK-YTO-TR 176, Radiation and Nuclear Safety Authority, Helsinki, 2001.
3. T. Ueno, K. Azumi and M. Seo, *J. Electroanal. Chem.* **540**, 97 (2003).
4. I. Betova, B. Beverskog, M. Bojinov, P. Kinnunen, K. Mäkelä, S.-O. Petersson, and T. Saario, *Electrochem. Solid State Lett.* **6**, B19 (2003).
5. B. Rosborg, O. Karnland, G. Quirk, and L. Werme, in Proceedings of the International Workshop "Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems", EFC event N° 256, 26–29 November, 2001, Cadarache, France (CD-ROM publication).