

ON-LINE MONITORING OF COPPER CORROSION AND REDOX CONDITIONS IN COMPACTED BENTONITE

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In STUK this study was supervised by Jussi Heinonen

The conclusions presented in the STUK report series are those of the authors and do not necessarily represent the official position of STUK

ISBN 951-712-877-0 (print)

ISBN 951-712-878-9 (pdf)

ISSN 0785-9325

Dark Oy, Vantaa/Finland 2004

KINNUNEN Petri, SAARIO Timo, BETOVA Iva (VTT Industrial Systems). On-line monitoring of copper corrosion and redox conditions in compacted bentonite. STUK-YTO-TR 206. Helsinki 2004. 20 pp.

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

Abstract

In the present work, the effect of the degree of bentonite compaction on Cu corrosion and redox conditions in bentonite has been studied. 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 conditions simulating those in a nuclear waste repository. Two tests extending for one month each have been performed. As a result, it can be stated that both developed sensors have proven to be reliable for long-time measurements. The increasing degree of compaction has been found to decrease the rate of Cu corrosion. In addition, it has been demonstrated that after an initial transient period of ca. 100 h, Cu corrosion in compacted bentonite practically stops. At the same time, the corrosion potential of Cu is still in the active corrosion region according to thermodynamic calculations. This is most probably due to the effect of copper containing redox systems in the vicinity of the copper surface on the corrosion potential. Furthermore, redox potentials in the free electrolyte remain rather high, which indicates a release of impurities from bentonite and their reactions on the Pt surface.

KINNUNEN Petri, SAARIO Timo, BETOVA Iva (VTT Tuotteet ja tuotanto). Kuparin korroosion ja hapetus-pelkistysolosuhteiden on-line monitorointi kompaktoidussa bentoniitissa. STUK-YTO-TR 206. Helsinki 2004. 20 s.

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

Tiivistelmä

Tässä työssä on tutkittu bentoniitin kompaktointiasteen vaikutusta kuparin korroosioon ja hapetus-pelkistysolosuhteisiin bentoniitissa. Kahden sensorin – on-line korroosionopeussensorin ja modifioidun referenssielektrodin – käytettävyyttä on testattu mittaamalla kuparin korroosiota ydinjätteen loppusijoituspaikkaa simuloivissa olosuhteissa kahdessa yhden kuukauden mittaisessa kokeessa. Tulokset osoittavat, että kumpikin sensori toimii luotettavasti pitkäaikaisissa kokeissa. Bentoniitin kompaktointiasteen lisäämisen on havaittu hidastavan kuparin korroosiota. Lisäksi kokeissa on havaittu, että kuparin korrosio kompaktoidussa bentoniitissa pysähtyy ensimmäisten sadan tunnin jälkeen. Toisaalta termodynaamisten arvioiden mukaan kuparin korroosio-potentiaali on kuitenkin samaan aikaan aktiivisen korroosion alueella. Tämä todennäköisesti johtuu siitä, että kuparia sisältävien hapetus-pelkistysparien läsnäolo lähellä kuparielektrodin pintaa nostaa kuparin korroosio-potentiaalia. Lisäksi hapetus-pelkistysolosuhteita vapaassa elektrolyytissä mittaavan platinan potentiaalin on mittauksissa havaittu olevan melko korkealla, mikä johtunee bentoniitista vapautuvista epäpuhtauksista ja niiden reaktioista platinan pinnalla.

Foreword

The present report describes the results obtained in 2003 in the project “Corrosion analysis of the copper canister”, that is a part of the Finnish Research Programme on Nuclear Waste Management (KYT, 2002–2005) funded by the Radiation and Nuclear Safety Authority, STUK. At STUK this project has been supervised by Mr. Jussi Heinonen.

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1 Introduction

This project is a part of the research area “Release of radionuclides from repository” promoting the long-term safety of final disposal of nuclear waste. Copper canister is an essential barrier for the release of radionuclides.

Since 1996 VTT industrial Systems has coordinated a research programme, that has been funded by Finnish and Swedish nuclear safety authorities STUK and SKI, concentrating on the durability of copper canisters in different corrosive environments. The copper canister designed for the waste disposal can be damaged in use in two different ways, either mechanically or due to corrosion. The mechanical failure of the copper canister may be caused for example by the tectonic movement or uneven wetting and following swelling of bentonite. The corrosion failure, on the other hand, may be caused by three different mechanisms, namely general corrosion, pitting corrosion or stress corrosion cracking.

The factors affecting the occurrence of different corrosion failures have been studied extensively especially in Finland, Sweden and Canada during the last decade. As a result, some possible failure mechanisms (e.g. stress corrosion caused by the nitrites) have been found not to be relevant in the expected Scandinavian final disposal environment, while others, such as the localised corrosion caused by sulphides, are still to be studied.

At the same time with the studies several

theoretical models have been presented to predict the corrosion phenomena of copper. Unfortunately no model that could comprehensively explain all the noticed features or different aspects that have to taken into account when considering the corrosion of copper canister has been presented up to date.

General corrosion of the copper canister will occur in groundwater. Thus, it remains to prove that the corrosion rate at all times remains below what can be accepted (e.g. $0.5 \mu\text{m a}^{-1}$) or alternatively that the overall extent of corrosion does not exceed the thickness of the canister wall, even though at some point in time the corrosion rate may markedly exceed the accepted average level. For this purpose, a reliable probe capable of measuring the corrosion rate of copper on-line in closely simulated final disposal conditions is needed.

In this project the on-line sensor for monitoring the general corrosion of copper developed in the Finnish Research Programme on Nuclear Waste Management (KYT) in 2002 [1] has been further modified and its long-term stability tested. The sensor has been used to monitor the effect of the degree of compaction of bentonite on the corrosion rate of copper in two tests extending for one month. In addition, a novel reference electrode design for monitoring potentials in the final disposal conditions in compacted bentonite has been developed and tested.

2 Goals

The goal of this work is to perform long-term corrosion rate monitoring tests of Cu in simulated final nuclear waste repository in the presence of wetted and compacted bentonite. 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.

3 Description of the target

The target of the present project is to study the effect of the degree of compaction of bentonite on the corrosion rate of copper and to verify the long-term stability of a modified reference electrode and an on-line corrosion sensor developed in previous work [1].

The existing external pressure balanced AgCl/Ag reference electrode design has to be modified to allow potential measurements in the presence of highly hydrophilic compacted bentonite. To this end, a design featuring a salt bridge between the modified AgCl/Ag reference couple and the stud-

ied copper specimens embedded in compacted bentonite has to be proposed. In such a configuration the reference electrode can be located outside the pressurised autoclave.

The resistance probe for on-line corrosion rate monitoring allows the use of pure copper as the sensor material and also 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 Methods

4.1 Environment

In this project the previously designed electrode configurations to measure the corrosion and redox-potential, as well as the corrosion rate of copper in the presence of compacted MX-80 bentonite have been applied to long-term experiments extending for one month. A scheme of the measurement set-up is shown in Fig. 1. The experiments are performed in highly saline groundwater (HSGW) with chloride content of ca. 53800 mg/l (1.52 M) in a static Ti-clad autoclave at a temperature of 80°C. The exact composition of HSGW is shown in Table I. The pressure of the autoclave has been adjusted to be the same as that of the compacted bentonite, i.e. ca. 4.5 and 10 MPa in the first and second experiment, respectively. Groundwater has been deoxygenated by purging the solution with N₂ gas (99.999%) further purified using an Oxisorb gas purification system. The resulting oxygen content of the purging N₂ gas after purification is less than 5 ppb in the gas phase, result-

Table I. Composition of the highly saline groundwater (HSGW) (mg/l).

Cl ⁻	SO ₄ ²⁻	Mg ²⁺	Ca ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻
53800	1200	700	9900	22700	190	4.8

ing theoretically in dissolved oxygen content of 0.2 ppt in groundwater (practically to 0.02 ppb [2]).

4.2 Materials and electrodes

The measurements were performed in a Ti-clad autoclave inside which a smaller vessel made of Zr as well as a Pt sheet to measure the redox potential of groundwater and a *conventional* pressure balanced AgCl/Ag reference electrode were installed. The conventional AgCl/Ag reference electrode has been used to check the stability of the modified AgCl/Ag reference electrode. The Zr vessel contains the compacted bentonite, a Cu wire probe to measure the corrosion rate, two weight loss coupons and a Pt wire to measure the redox potential in the bentonite (Fig. 1).

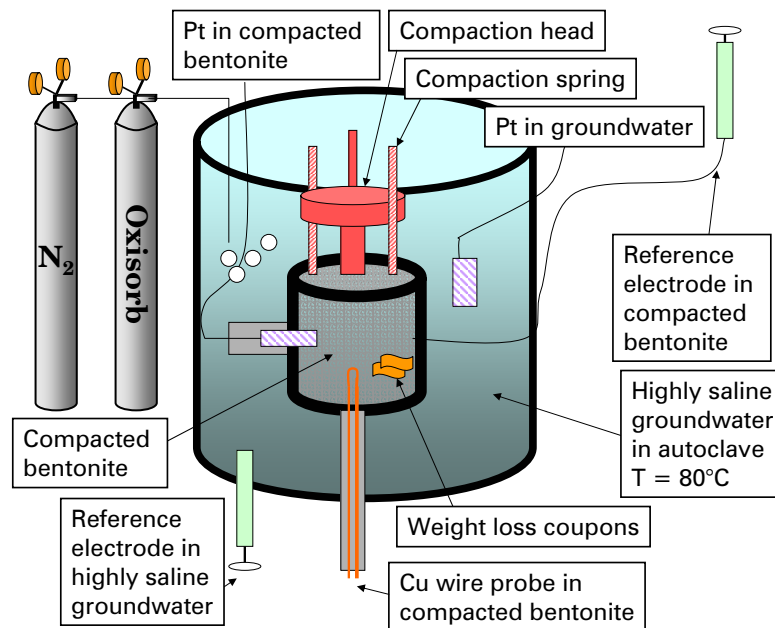


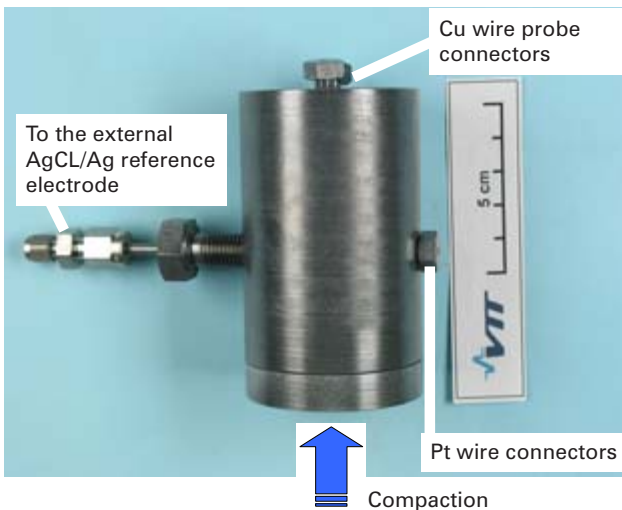
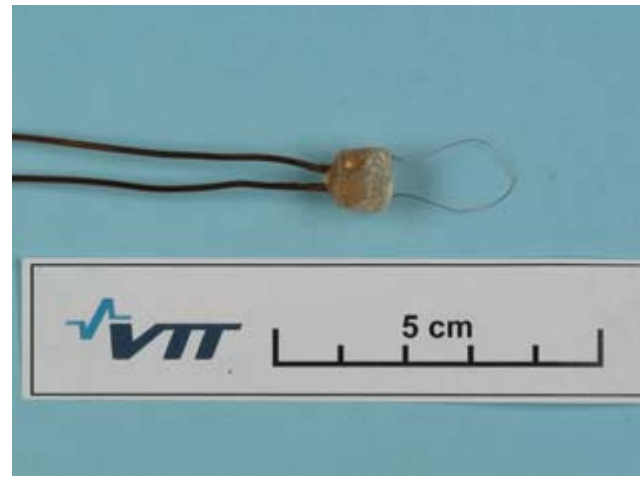
Figure 1. Scheme of the measurement set-up.

Table II. Composition (in ppm) of the test materials.

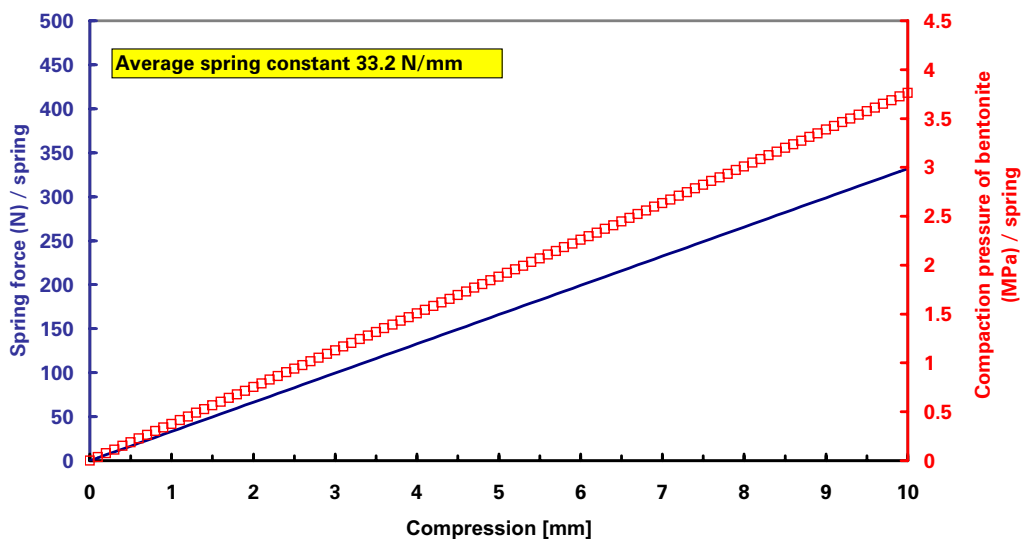
	Ag	Al	Bi	Ca	Fe	Mg	Mn	Na	Pb	Si	P	O
Cu99.99% Goodfellow	7	1	<1	<1	1	<1	<1	<1	<1	2	NA	NA
Cu-OPF	NA	NA	NA	NA	2	NA	NA	NA	NA	NA	45	1.5

A detailed picture of the Zr vessel inside the Ti-clad autoclave is shown in Fig. 2 and that of the Cu wire probe in Fig 3. The resistance wire probe was manufactured from copper wire with a diameter of 0.125 mm acquired from Goodfellow Ltd. The composition of the material is shown in Table II. Bentonite was mixed with the highly saline groundwater and soaked at room temperature for more than 10 h before compaction. The

force to compact the bentonite in the Zr vessel is produced using springs along which the lid of the vessel is moved. The measured spring constant for each spring is ca. 33.2 N/mm (Fig. 4). Two different degrees of compaction have been used to check if the degree has any influence on the corrosion rate of copper. The first measurement has been performed using three springs with compression of 3.5 mm corresponding to calculated pressure of

**Figure 2.** Zr vessel used for on-line corrosion rate measurements in compacted bentonite.**Figure 3.** Cu wire probe used for on-line corrosion rate measurements in compacted bentonite.

Compaction force and pressure of bentonite

**Figure 4.** Measured force of a spring used to compact bentonite as well as the calculated compaction pressure of bentonite as a function of spring compression.

ca. 1.3 MPa/spring and total compaction pressure of ca. 4.5 MPa. In the second run the compression has been 4.5–5 mm and the number of springs six, producing a total calculated compaction pressure of ca.10 MPa to bentonite.

In addition to the Cu wire probe two weight loss coupons made of oxygen-free phosphorus microalloyed copper (Cu-OFP) were installed to the Zr vessel. The composition of Cu-OFP is shown in Table II.

The modified AgCl/Ag electrode consists of another Zr vessel outside the Ti-clad autoclave containing groundwater and a AgCl/Ag reference pair (see Fig. 5). This vessel is connected to the Zr vessel containing bentonite and Cu specimens via a stainless steel tube, that is filled with compacted bentonite and groundwater. The pressure in the reference electrode vessel is the same as in the Ti-autoclave and the temperature is room temperature. The advantage of this reference electrode configuration is that it is easy to install and maintain. In this project the operation of this

reference electrode configuration has been checked by measuring its potential versus the conventional pressure balanced AgCl/Ag reference electrode located in the Ti-clad autoclave filled with highly saline groundwater.

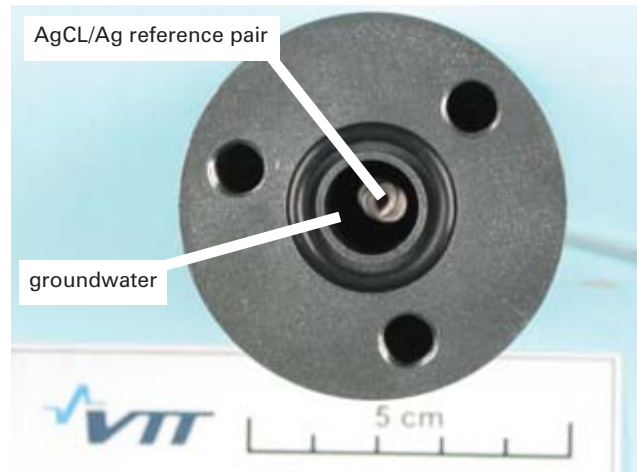


Figure 5. Modified AgCl/Ag electrode to measure the potentials of Cu specimens in the compacted bentonite.

5 Results and discussion

5.1 Depth of corrosion penetration of Cu, corrosion and redox potentials at a compaction pressure of 4.5 MPa

The first 1 month test was performed with a bentonite compaction pressure of 4.5 MPa. The measured corrosion depth penetration and corrosion rate of Cu are shown in Fig. 6a and the potential of the Cu corrosion probe as well as the potential of Pt in the highly saline groundwater and in bentonite in Fig. 6b. The results have been shown vs. the modified AgCl/Ag reference pair, that is connected to the Zr vessel containing Cu samples via a salt bridge formed by HSGW and bentonite. The difference in potential between the modified reference electrode filled with the highly saline groundwater and the conventional reference electrode filled with 0.505 M KCl has been measured to be ca. 0.08 V at 80°C. Based on this, the conversion factor of the potentials measured with the modified reference electrode to the SHE scale is ca. 0.12 V.

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

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

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 instantaneous corrosion rate as

$$\Delta_{\text{corr}} = 0.5r_0 \sqrt{\frac{R_0}{R}} \frac{1}{R} \frac{dR}{dt} \quad (2)$$

When calculating the corrosion depth penetration it has to be recognised that the specific resistivity of the Cu wire changes as a function of tempera-

ture. This change can to be taken into account so that the “real” initial wire resistance (R_0) in Eq. (1) is selected to be the value of the wire probe in the end of the heating period from 25°C to 80°C. Of course, corrosion reactions take place also during the heating period, but it can be estimated that the change in the wire resistance caused by the corrosion reactions during the heat-up is negligible in comparison to the change caused by temperature.

As seen in Fig. 6a, the corrosion of Cu takes place mainly during the first 100 hours. This is a much longer time than what has been measured previously (5–8 h) in wetted uncompacted bentonite [1]. The reason for this difference may be that in compacted bentonite the decomposition of the oxygen contained in the gas-filled pores of the bentonite is slower and therefore it takes longer time for the Cu corrosion to level off. The first 24 hours of the measurement have been performed at room temperature after which the heating of the Ti-clad autoclave has been started. It has been noticed that after compaction into the Zr vessel the pre-wetted bentonite is not in stable condition but slowly flows for some time giving out a small quantity of water. This results in lengthening of springs from their initial position and thus decrease in the compaction degree. Because of this, during the room-temperature period the compaction of bentonite has been adjusted to a stable value by tightening the springs until the flow stops. This stabilisation of bentonite typically has taken place in 24 hours. The Cu corrosion takes place mostly during room-temperature and heating periods and levels off after 100 h, resulting in a total corrosion penetration of about 0.0011 mm (1.1 μm). The latter fact means that Cu corrosion rate is practically zero at exposure times exceeding 100 h. After ca 200 h of exposure the depth of corrosion penetration seems to even slightly de-

crease, which may be caused by redeposition of Cu. However, the signal coming from the Cu wire sensor fluctuates to some extent during the whole measurement period, which may be caused by small changes in temperature during the measurement. It can be estimated that a change of one degree of temperature changes the resistance of the Cu wire ca. 0.43%. In addition, this change in resistance would correspond to a change of ca. 0.14 μm in the corrosion depth penetration. From the results shown in Fig. 6a, the fluctuation can

be calculated to be of the order of 0.07 μm , which corresponds to a change of ca. 0.5 centigrades in temperature. This is a normal accuracy of temperature control in high-temperature autoclave measurements. As a consequence of this small temperature fluctuation, the calculated instantaneous corrosion rate also shows some fluctuation due to the fact that the derivative term including the change in resistance in corrosion rate equation (Eq. 2) is very sensitive to temperature fluctuations. Therefore, the fluctuation in the instantane-

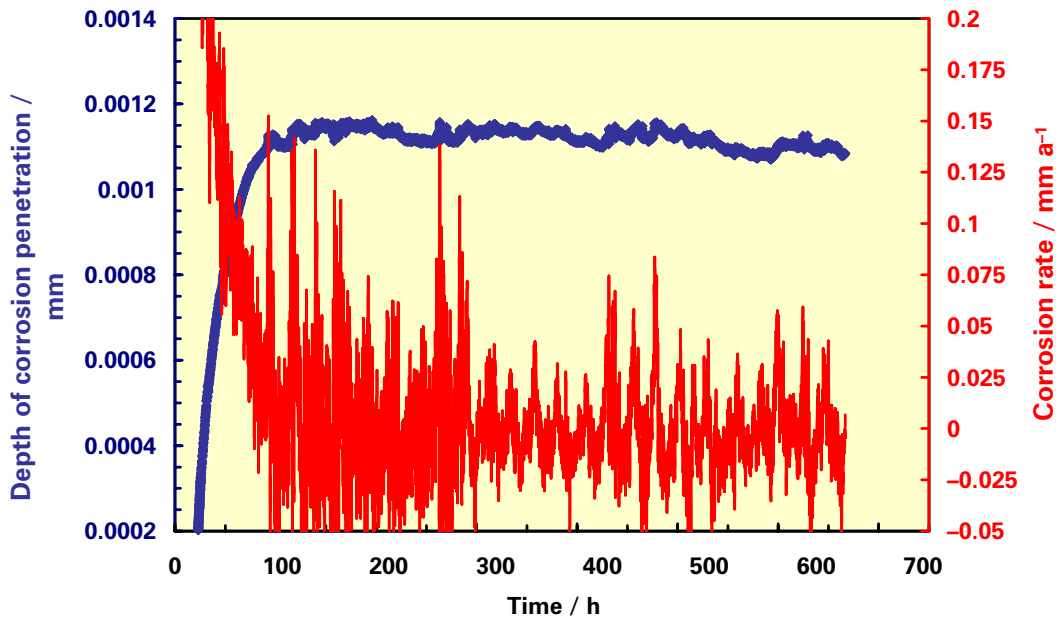


Figure 6a. Corrosion depth and instantaneous corrosion rate of Cu in compacted bentonite (degree of compaction 4.5 MPa) during the 1 month test.

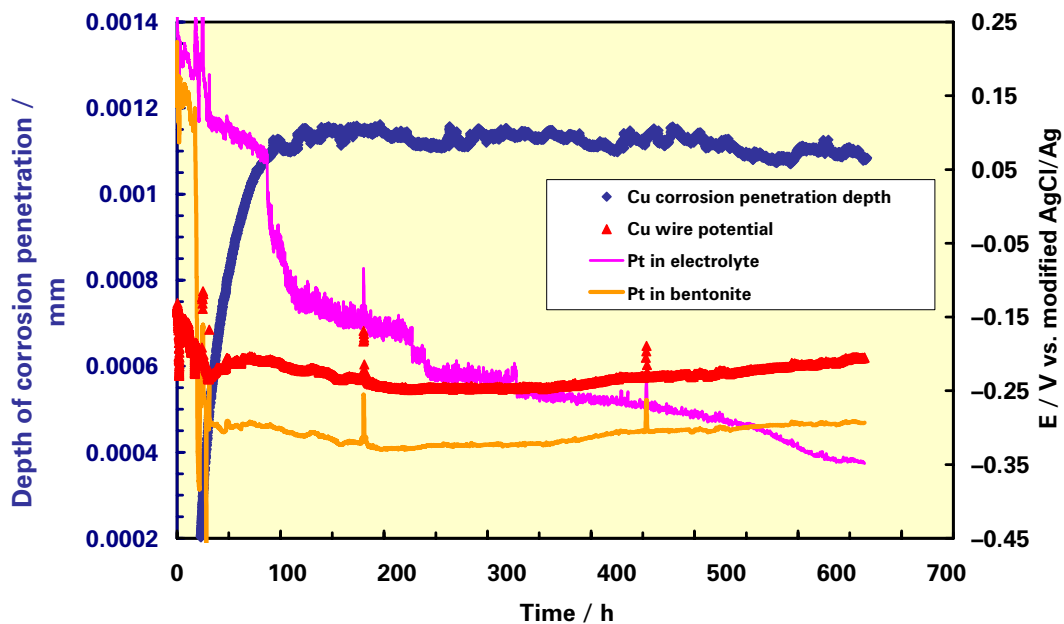


Figure 6b. Corrosion depth of Cu in compacted bentonite (degree of compaction 4.5 MPa) and potentials of Cu corrosion probe, as well as Pt in highly saline groundwater and in bentonite during the 1 month test.

ous corrosion rate after 100 hour exposure time can be said to be purely due to the temperature fluctuation and the calculation procedure, and the average corrosion rate is zero. In overall, the measurement result is almost similar to that obtained previously in wetted uncompact bentonite [1].

The potential of the Cu probe in compacted bentonite with the compaction pressure of 4.5 MPa stays between -0.2 and -0.25 V vs. modified AgCl/Ag (-0.08 ... -0.13 V_{SHE}) for the whole experiment after the heat-up showing a slightly increasing trend towards the end of the test (Fig. 6b). According to the theoretical equilibrium calculations [4, 5] these potential values are close to the equilibrium potential of the relevant copper containing redox system (e.g. $\text{CuCl}_3^{2-}/\text{Cu}$ redox pair). These potential values are, however, higher in comparison to our earlier tests in simulated groundwater without bentonite [6, 7] as well as in wetted uncompact bentonite [1]. One possible explanation for this feature may be that in compacted bentonite the diffusion of copper-containing species away from the wire is slower and thus the content of ionic Cu-species close to the wire stays higher, resulting in a higher potential. However, the total change of the Cu wire potential, ca. 0.04 V, can be considered to be relatively small.

The potential of Pt in compacted bentonite follows that of the Cu probe during the whole measurement period showing values roughly 0.08 V lower than that of the Cu probe (Fig. 6b). These rather high potential values for Pt indicate that some residual oxygen probably exists in the bentonite after compaction. Also the existing ionic Cu species can increase the potential of Pt. The potential value of Pt in bentonite is close to that obtained earlier in wetted uncompact bentonite [1].

We have previously shown in pure water without Cu or any other soluble species that the purging procedure used removes oxygen from the solution very efficiently [2]. Thus, the slow decrease of the potential of Pt in the free electrolyte (see Fig. 6b) is most probably due to impurities in the solution released from the bentonite. The Pt potential reaches a value of ca. -0.35 V vs. modified AgCl/Ag, (-0.23 V_{SHE}) after 660 h, which is almost similar to that obtained in wetted uncompact bentonite [1].

5.2 Depth of corrosion penetration of Cu, corrosion and redox potentials at a compaction pressure of 10 MPa

The second test was performed with a bentonite compaction pressure of 10 MPa (Figs. 7a and 7b). The test has been carried out so that the small Zr vessel, in which the Cu probe and the weight loss coupons are located, has been opened after the first test, the coupons have been weighed and re-polished, after which the vessel has been closed and the compaction performed. The bentonite and the Cu wire probe inside the vessel have not been changed between the measurements. During the polishing of Cu coupons, however, oxygen has been able to penetrate inside the Zr vessel and to bentonite.

The depth of Cu corrosion penetration stabilises rather quickly after the heat-up period and reaches a level of 0.83...0.89 μm , which is roughly 80% of the level obtained at 4.5 MPa compaction pressure (Fig. 7a). The corrosion depth penetration level seems to be rather stable through the rest of the test indicating that no further Cu corrosion takes place. This can be also confirmed by corrosion rate calculations, which show an average corrosion rate of zero mm a^{-1} . Again, however, the values of the instantaneous corrosion rate fluctuates rather much due to small temperature fluctuations (less than one $^\circ\text{C}$), which affects the measured resistance of the Cu probe and accordingly the differential corrosion rate calculation procedure (see above).

The potential of the Cu probe seems to increase during the whole experiment; between 0...100 h quite rapidly but after 100 h in a slower fashion and reaches the value of ca. -0.24 V vs. modified AgCl/Ag (-0.12 V_{SHE}) at the end of the test (Fig. 7b). This value is almost the same as at the end of the first measurement (see. Fig. 6). The total increase of the Cu wire potential, ca. 0.03 V, is relatively small and may be explained again the slower diffusion of copper-containing species away from the wire or some other processes close to the Cu probe, which results in a higher potential of the probe.

The potential of Pt in bentonite shows a fast decrease during the heat up period and then follows roughly the trend of the Cu probe potential, except in the beginning of the test, between 0...100h, where the rate of increase is smaller

(Fig. 7b). The final potential, -0.32 V vs. modified AgCl/Ag (-0.20 V_{SHE}) is almost the same as in the first test.

The potential of Pt in the free electrolyte, after a small initial increase, decreases during the whole experiment reaching a value of -0.32 V vs. modified AgCl/Ag (-0.20 V_{SHE}) at the end of the

test (Fig. 7b). However, the increase of the potential of Pt in the free electrolyte during and immediately after the heat-up period is much lower than in the first test and the maximum potential is ca. -0.22 V vs. modified AgCl/Ag (-0.10 V_{SHE}) obtained at around 60 h.

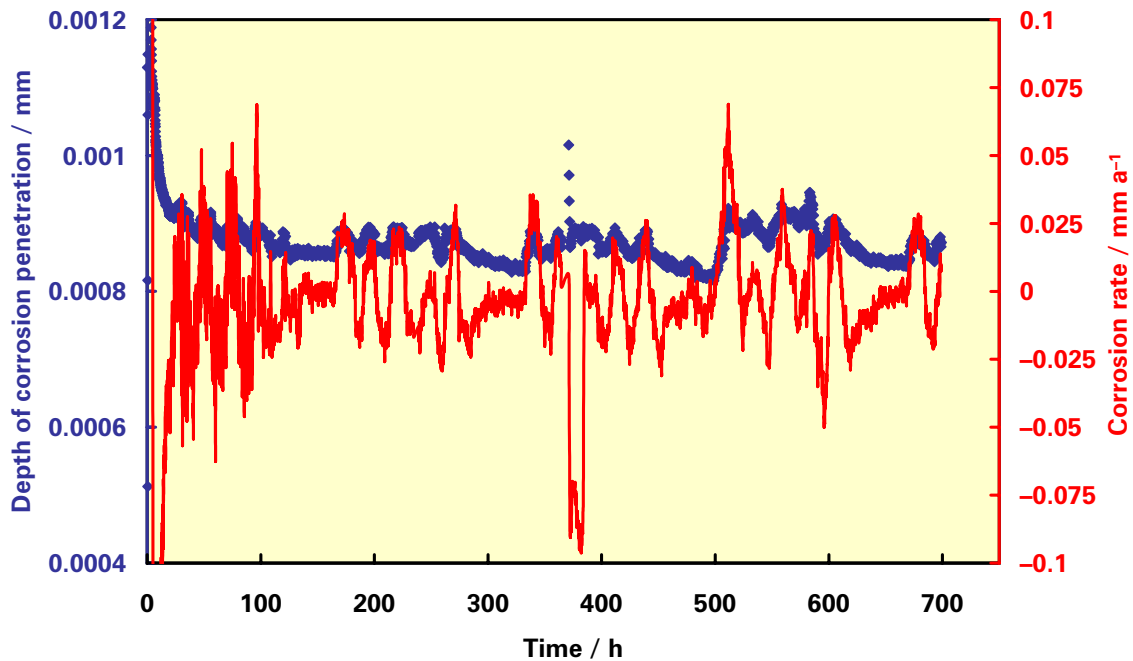


Figure 7a. Corrosion depth and instantaneous corrosion rate of Cu in compacted bentonite (degree of compaction 10 MPa) during the 1 month test.

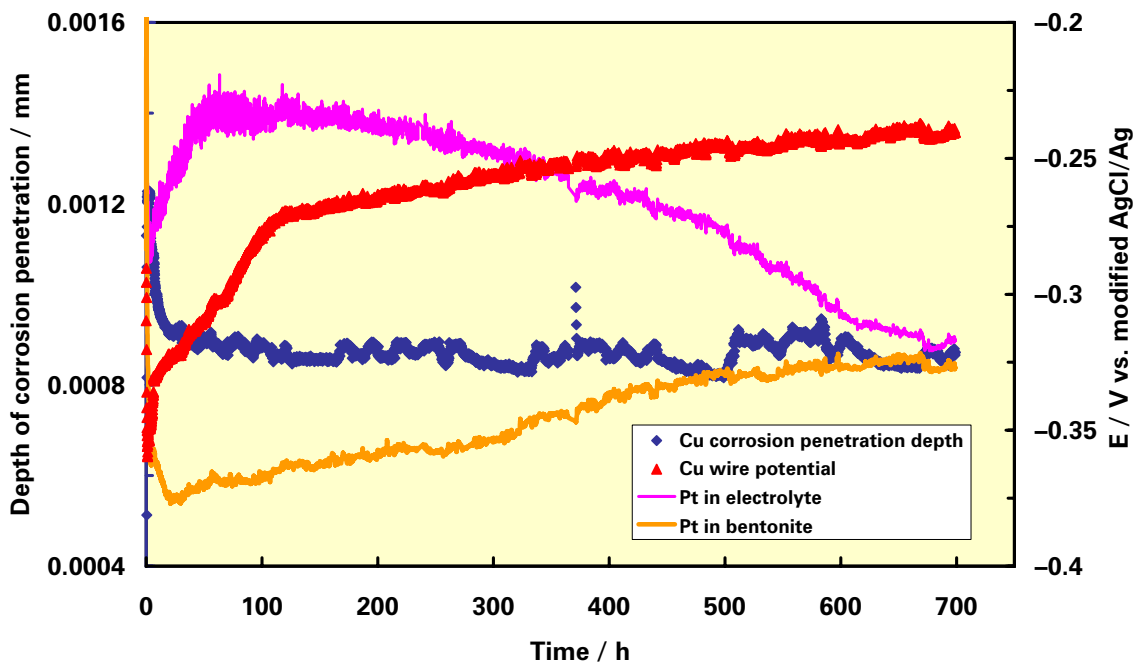


Figure 7b. Corrosion depth of Cu in compacted bentonite (degree of compaction 10 MPa) and potentials of Cu corrosion probe as well as Pt in highly saline groundwater and in bentonite during the 1 month test.

5.3 Weight loss coupon results

Two weight loss samples were exposed to the environment in the compacted bentonite in both tests. The weight loss of the specimens showed an average 1.0 mg (0.9 mg and 1.1 mg) in the first test (compaction pressure 4.5 MPa) and 0.35 mg (0.4 mg and 0.3 mg) in the second test (compaction pressure 10 MPa). The general corrosion rate can be calculated from the weight loss using the formula

$$\Delta = \frac{\Delta m \cdot 3650}{\rho \cdot A \cdot t} [mm/y] \quad (3)$$

where Δm = weight loss [g], ρ = density [$g\ cm^{-3}$], A = surface area [cm^2] and t = exposure time [days]. The density of copper is $8.94\ g\ cm^{-3}$. The calculated corrosion rate is $0.0047\ mm\ y^{-1}$, i.e. $4.7\ \mu m\ y^{-1}$, in the first test and $0.0014\ mm\ y^{-1}$, i.e.

$1.4\ \mu m\ y^{-1}$, in the second test. This corrosion rate is clearly higher than the acceptable average corrosion rate, $0.5\ \mu m\ y^{-1}$. However, the most likely explanation for this result is that the corrosion takes place mainly in the beginning of the test as shown by the on-line corrosion probe data (see Figs. 6 and 7). According to the weight loss coupon tests the increase of the bentonite compaction degree from 4.5 MPa to 10 MPa decreases the corrosion rate roughly by a factor of three, which is less than estimated from the data measured with the on-line corrosion probe (a factor of about six). However, these values are still reasonably close to each other.

The surfaces of the weight loss coupons have been visually examined for the presence of pitting corrosion. No indications of pitting have been found.

6 Conclusions

The following conclusions regarding the effect of bentonite on the Cu corrosion and the development work of the sensors can be drawn:

- The developed on-line Cu corrosion rate measurement procedure is suitable for the monitoring of the effect of the degree of bentonite compaction on the general corrosion of copper. In addition, the developed reference electrode configuration offers a reliable method for monitoring the corrosion potential of Cu as well as the redox conditions both in HSGW and in compacted bentonite.
- However, to be able to obtain the planned compaction level of bentonite (>50 MPa), the compaction procedure developed in this work still needs some modification.
- The corrosion process detectable by the probe stops after ca. 100 h from the immersion to the compacted bentonite. The resistance signal was followed up to at least 670–700 h in two successive test runs. Both the on-line monitoring of Cu corrosion and the weight loss coupon measurements indicate that the Cu corrosion rate decreases when the degree of compaction of bentonite is increased from 4.5 MPa to 10 MPa.
- The potential of platinum in the compacted bentonite showed a slightly increasing trend in both measurements for most of the time. The suggested reason for this trend is the accumulation of the copper containing redox species released from the copper wire in compacted bentonite.
- In the free electrolyte the potential of Pt, however, decreases during the measurement after the heat-up period. A possible reason for this trend may be reactions of impurities in the electrolyte on the Pt surface.
- The reference electrode developed in this work has been found to be more stable and reliable than the one tested previously [1]. The electrode configuration is easy to install and maintain and shows values that are in accordance to previous experiments.

7 Summary

In the present work, the effect of the degree of bentonite compaction on Cu corrosion and redox conditions in bentonite has been studied. 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 conditions simulating those in a nuclear waste repository. Two tests extending for one month each have been performed. As a result, it can be stated that both developed sensors have proven to be reliable for long-time measurements. The increasing degree of compaction has been found to decrease the rate of Cu corrosion. In addition, it has

been demonstrated that after an initial transient period of ca. 100 h, Cu corrosion in compacted bentonite practically stops. At the same time, the corrosion potential of Cu is still in the active corrosion region according to thermodynamic calculations. This is most probably due to the effect of copper containing redox systems in the vicinity of the copper surface on the corrosion potential. Furthermore, redox potentials in the free electrolyte remain rather high, which indicates a release of impurities from bentonite and their reactions on the Pt surface.

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