

Corrosion of Copper in 1 M NaCl under Strictly Anoxic Conditions

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ABSTRACT

The corrosion of copper in 1 M NaCl has been investigated at room temperature and at 80°C by an on-line resistance probe, solution analysis of dissolved copper and weight loss measurements. At room temperature, corrosion of the copper as indicated by an increase of the probe resistance has been detected during the first 60-80 h of exposure. After the corrosion potential has reached the immunity region of Cu, a decrease in the resistance of the sensor is observed, probably due to redeposition of Cu from the solution. It can be concluded that the corrosion of copper at room temperature virtually stops after 60-80 h due to the anoxic conditions established in the experiments. The similarity in the trends of the corrosion and redox potential during exposure seems to indicate that Cu(II) contained in the native oxide on Cu and/or formed by homogeneous oxidation of Cu(I) during the initial oxic period of exposure acts as a redox-agent determining the chemical conditions in the closed system.

INTRODUCTION

In the present Scandinavian design, spent nuclear fuel is planned to be packed in a cast iron canister with an outer copper shield for corrosion protection. The 50 mm thickness of the wall of the copper canister sets a limit of $0.5 \mu\text{m y}^{-1}$ for the maximum corrosion allowance of copper at a predefined lifetime of 10^5 years.

It is possible that general corrosion of copper occurs in deep repository conditions. Thermodynamic calculations [1] indicate a possibility of copper corrosion in highly saline water environments of the anoxic type (concentration of oxygen $<10^{-6} \text{ mol l}^{-1}$ [2]). In accordance with such predictions, corrosion rates several times higher than $0.5 \mu\text{m y}^{-1}$ have been measured for copper in saline groundwaters in short-term experiments [3,4]. Long-term field experiments [5] have also indicated unacceptably high corrosion rates of copper in deep repository conditions.

The aim of the present work has been to quantify the extent of copper corrosion in 1 M NaCl in oxygen-free conditions using three methods: an online sensor based on the measurement of the resistance of a copper wire probe, weight loss coupons and solution analysis. A secondary goal has been to find out whether the potential of copper will reach the level of redox potential estimated to prevail in the undisturbed ground water ($E_{\text{H}} = -0.3 \dots -0.4 \text{ V}_{\text{SHE}}$) when the dissolved oxygen content is negligibly low.

EXPERIMENTAL DETAILS

Weight loss coupons (area 14 cm^2) made of oxygen-free phosphorus microalloyed copper (Cu OFP, 45 ppm P and 1.5 ppm O), a Pt-electrode and a AgCl/Ag reference electrode filled with 1 M NaCl were placed in a 5 L Ti-autoclave together with a resistance probe made of Cu (99.95%),

Goodfellow, diameter 0.125 mm, length 45 mm). A dc current of 85 mA was fed through the probe and the resulting voltage drop was continuously recorded to monitor the wire probe resistance. 1 M NaCl was used as electrolyte at $23\pm 1^\circ\text{C}$ and 1 MPa N_2 overpressure or $80\pm 1^\circ\text{C}$ and 14.0 MPa N_2 overpressure. The electrolyte volume was 2.5 L at room temperature and 4.5 L at 80°C . In the experiments at room temperature, a glass vessel filled with electrolyte was installed in the autoclave. Dissolved oxygen was removed by nitrogen gas purified using an Oxisorb R 200 oxygen scavenger system resulting in $\text{O}_2 < 5$ ppb in the autoclave inlet gas. The Cu-coupons and the Cu resistance probe were cathodically polarised by a potentiostat during the initial oxidic period in the room-temperature experiments.

RESULTS

Experiments at 80°C

The first test was performed without the Oxisorb system (probable steady state concentration of dissolved oxygen of about 10-20 ppb). Fig. 1a shows that the resistance of the Cu-wire probe increased rapidly during the initial period of solution deaeration by N_2 bubbling (about two hours) and continued to increase, albeit more slowly, for the rest of the exposure. Finally, the wire was broken off by corrosion after about 3.5 days. The corrosion rate can be estimated to be higher than $100\ \mu\text{m day}^{-1}$ in the first stage and $1.5\ \mu\text{m day}^{-1}$ in the latter stage. The increase from about 0.11 to $0.13\ \Omega$ is caused by the increase of the temperature to 80°C . The potential of the Cu-flag stabilised at about $-0.18\ \text{V}_{\text{SHE}}$ and that of Pt decreased slowly to about $-0.15\ \text{V}_{\text{SHE}}$. The solution pH (measured from ex situ samples) was in the beginning 6.4 and at the end of the experiment 9.9. A value of $48\ \mu\text{m y}^{-1}$ was obtained for the average corrosion rate on the basis of the weight loss measurements. A direct comparison between the corrosion rate values obtained from the weight loss coupons and the resistance probe was not possible in this case, because of the wire break. Solution analysis showed a cyclic variation of the dissolved Cu concentration between 800 and 1500 $\mu\text{g/l}$, suggesting a possible partial deposition of Cu onto the autoclave walls. The variation of the dissolved Cu concentration with exposure time indicates also the possibility of electrolyte stratification, as no stirring of the solution was performed.

The second test was performed otherwise similarly but with the Oxisorb system, so that the gas at the autoclave inlet had < 5 ppb of oxygen as impurity. Independent Pt electrode potential measurements in the same autoclave at 80°C in pure water without Cu electrodes (not shown for the sake of brevity) resulted in a value of the redox potential of $-0.44\ \text{V}_{\text{SHE}}$, which theoretically corresponds to a dissolved oxygen concentration less than 0.01 ppb.

The on-line results from the experiment with Oxisorb also show that during the initial period of solution deaeration, the resistance increased indicating rapid corrosion (Fig.1b). After oxygen removal the resistance almost levelled off, contrary to the behaviour in Fig.1a. At the same time, however, the corrosion potential of Cu stabilised at about $-0.2\ \text{V}_{\text{SHE}}$, only 0.02 V lower than without Oxisorb (Fig.1a-b). The redox-potential showed some fluctuation with an average value close to $-0.10\ \text{V}_{\text{SHE}}$. The pH measured from ex situ samples was 6.4 at the start and 9.5 at the end of the test.

The time variation of the depth of corrosion penetration, $d_{\text{corr}}(t)$, can be calculated by the formula [6]:

$$d_{\text{corr}}(t) = r_0 \left(1 - \sqrt{\frac{R_0}{R(t)}} \right) [\mu\text{m}]$$

where r_0 is the initial radius of the resistance probe, R_0 the initial resistance value and $R(t)$ is the resistance value at a certain time of exposure, t . Such data are presented in Fig. 2 with a logarithmic time scale to emphasise the initial period of exposure. The instantaneous corrosion rate, determined by numerical differentiation of the $d_{\text{corr}}(t)$ curve using a polynomial interpolation, is also shown in Fig. 2.

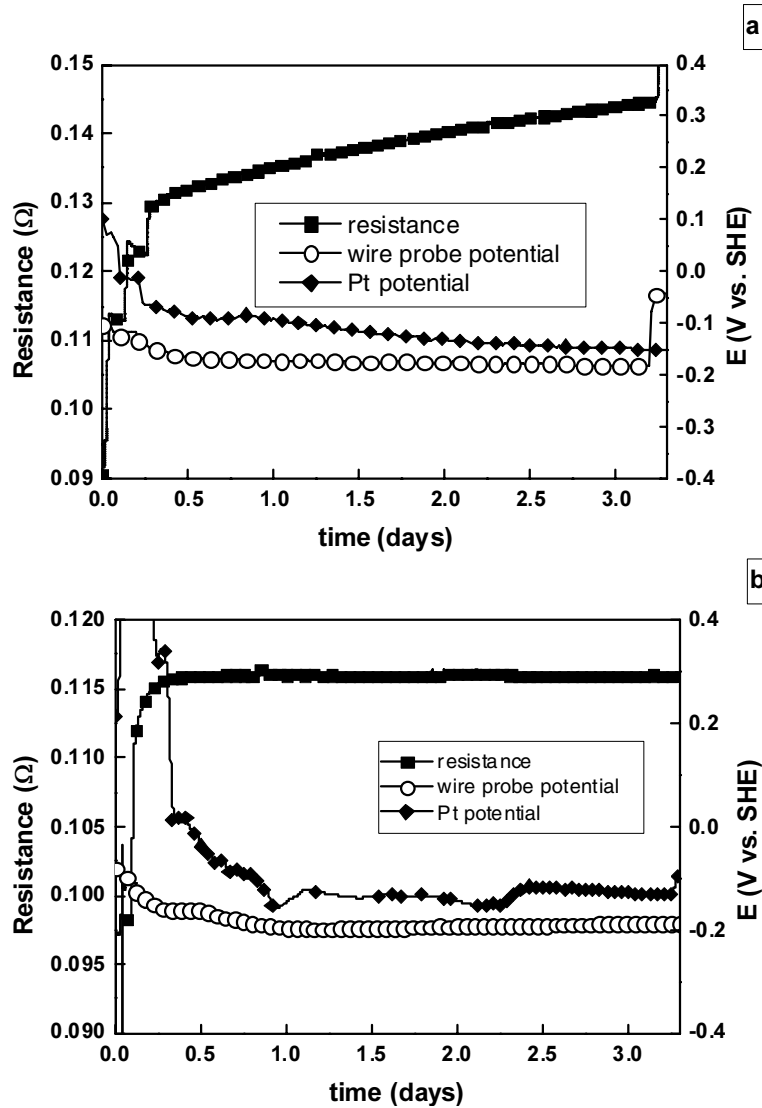


Figure 1. Evolution of the resistance of the Cu wire probe sensor, its corrosion potential and the potential of the Pt electrode (redox potential) during exposure at 80 °C without Oxisorb deaeration system (a) and with such a system (b).

Three periods can be identified in Fig. 2 - an initial period (0..0.5 h, i.e. 0.02 days) with very high corrosion rate (above $100 \mu\text{m d}^{-1}$), a second period (up to 6 h, or 0.25 days) during which the corrosion rate decreases significantly and a third period (up to 6 days) in which the corrosion rate is negligible. The solution analysis showed an initial rapid increase of Cu to about $1200 \mu\text{g/l}$ and a further slower increase to about $2300 \mu\text{g/l}$. The corrosion coupons showed a total weight loss of 14.6 mg, i.e. the average corrosion rate was $11.8 \mu\text{m y}^{-1}$. However, a steady state mass

balance of Cu could not be achieved, most probably due to copper deposition on the autoclave walls. To exclude the influence of the autoclave, further experiments were carried out in a glass vessel inserted in the autoclave at room temperature.

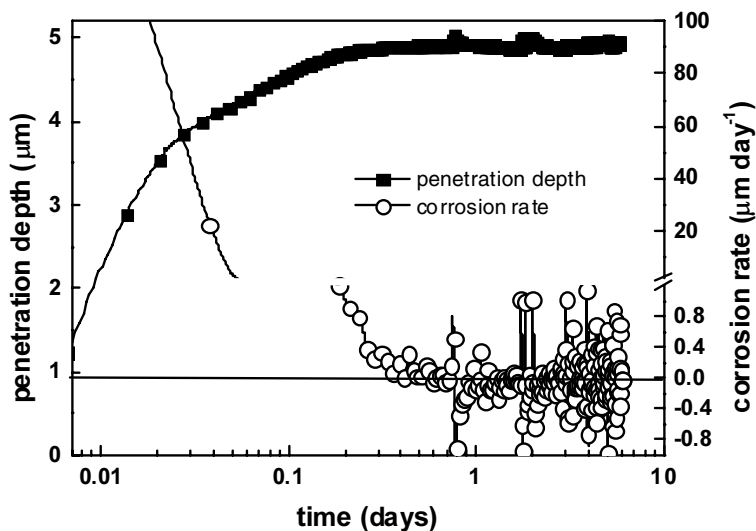


Figure 2. Penetration depth of corrosion (left ordinate) and differential corrosion rate (right ordinate) calculated from the resistance data. Note the logarithmic time scale.

Experiments at room temperature

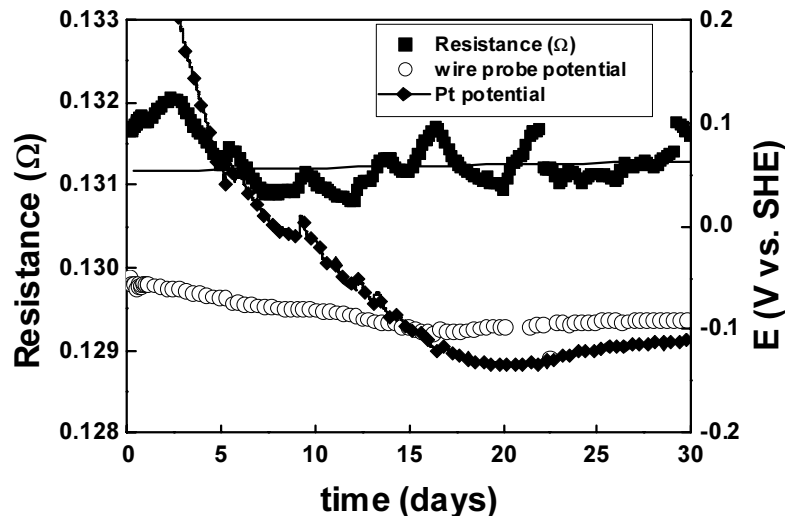


Figure 3. Evolution of the resistance of the Cu wire probe sensor, its corrosion potential and the potential of the Pt electrode with exposure time to 1 M NaCl at room temperature. Black line - mean value of the resistance between 4th and 30th day of exposure.

Figure 3 shows the resistance and the potential of the Cu-wire electrode during a 30-days exposure in 1M NaCl at room temperature. In analogy with the measurements at 80 °C, an initial very rapid increase of the resistance (not shown in the Figure) gradually levels off, and a maximum in the resistance is reached after roughly 2.5-3.5 days of exposure. After that the resistance starts to decrease indicating probably a deposition process. A closer look at Fig.3 shows that this behaviour is cyclic, and that the mean value of the resistance does practically not

change in the time period between the 7th and 30th day of exposure. This indicates that no net corrosion is detected by the sensor. Another plausible explanation for the cyclic change in resistance is a probable temperature fluctuation during exposure. The potential of the wire probe decreases with exposure, reaching a value of -0.1 V vs. SHE after ca. 15 days of exposure (Fig.3). This potential lies in the immunity region of Cu in 1 M NaCl at room temperature [7].

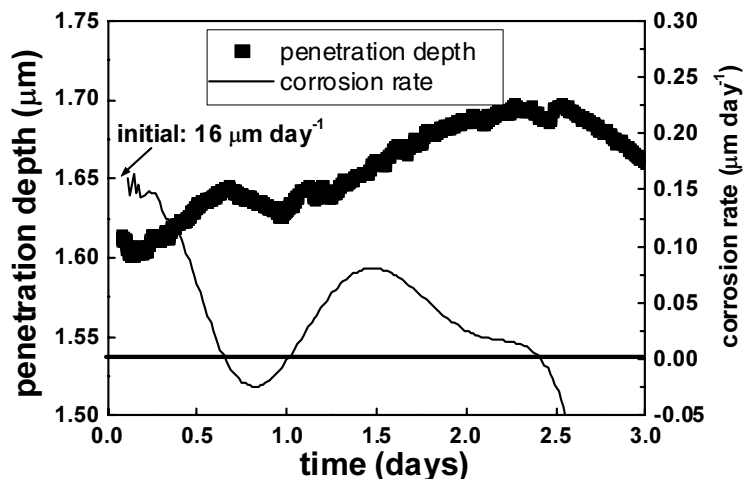


Figure 4. Penetration depth of corrosion (left ordinate) and corrosion rate, $\mu\text{m day}^{-1}$ (right ordinate) during the first 3 days of a room temperature experiment. The corrosion rate during the initial period of exposure is indicated by an arrow.

Fig. 4 shows the evolution of the corrosion depth with time during the first 3 days of exposure together with the differential corrosion rate. In analogy to the experiment at 80 °C with Oxisorb (Fig. 2), the corrosion rate during the initial period is very high, decreasing essentially to zero after 2.5 days of exposure (Fig.4). Solution analysis showed a high concentration of Cu (ca. 1000 $\mu\text{g l}^{-1}$) already at the 2nd day of exposure. The decrease in the concentration of dissolved Cu between 5 and 16 days was most probably due to unintentional electrolyte stratification. A value of 1390 $\mu\text{g l}^{-1}$ was reached after 30 days of exposure. The total amount of dissolved Cu was estimated to be 13.02 ± 0.08 mg, whereas the total weight loss of Cu was 12.1 ± 0.1 mg. Assuming that the total weight loss occurs during the first 5 days of exposure, we estimated the penetration depth of corrosion as 1.6 μm , in good agreement with the wire probe results. This simple calculation demonstrates that the average corrosion rate has been largely overestimated due to the very high initial corrosion rate.

DISCUSSION

The results of the online monitoring in this work demonstrate that copper corrosion virtually stops after 2.5-3.5 days of exposure at room temperature. Meanwhile, the potential of the Cu specimen reaches the immunity region (ca. -0.1 V vs. SHE) after ca. 10-15 days at room temperature. The potential of Pt in the solution is closely similar, which indicates that in a closed system a certain amount of Cu is deposited on Pt.

When a Cu electrode is immersed in the 1 M NaCl solution, dissolution of the native oxide proceeds and aqueous complexes of copper are formed. In a quiescent solution, soluble Cu(II) is probably not fully reduced to Cu(0), even though reduction is thermodynamically favoured at

very low oxygen levels. Alternatively, soluble Cu(I) can be oxidised by the remaining oxygen in the solution to Cu(II) in a homogeneous reaction [8] or disproportionation of Cu(I) to Cu(II) and Cu(0) can occur. The residual Cu(II) can act as oxidant during corrosion of Cu via its partial reduction to Cu(I). After the consumption of the most part of the oxygen, the potential of Cu reaches the immunity region. Deposition of metallic copper is assumed to occur resulting in the consumption of the [Cu(0)/Cu(I)] catalytic surface sites [9] and a further decrease in the oxygen reduction rate. As the residual concentrations of both oxygen and Cu(II) are very low, a very low corrosion rate (practically zero) will be maintained for a relatively long period.

CONCLUSIONS

The following main conclusions can be drawn from the present results:

- Copper corrodes with an appreciable rate during the initial few hours of exposure to 1 M NaCl containing very small amounts of oxygen. Subsequently, the corrosion rate decreases, being however noticeable up to 3-4 days of exposure at room temperature. For longer exposure times up to 30 days, the corrosion rate becomes negligible and back deposition of copper also occurs.
- The potential of copper at room temperature reaches the immunity region as predicted by thermodynamics after ca. 7-10 days of exposure. The exact determination of the Cu(I)/Cu(0) equilibrium line depends on the starting conditions via the steady state concentration of soluble copper.
- In a closed system containing soluble Cu, Pt electrodes can not be used to monitor reliably the redox potential because copper deposition on such electrodes transforms them into Cu-like electrodes.

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