



**Working Report 2003-45**

# **Corrosion of Copper in Anoxic 1M NaCl Solution**

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## CORROSION OF COPPER IN ANOXIC 1 M NaCl SOLUTION

### ABSTRACT

The corrosion behaviour of copper in 1 M NaCl has been investigated at room temperature and at 80 °C in oxygen-free conditions (estimated oxygen level 0.001-0.01 ppb). The extent of corrosion up to 30 days of exposure was followed by an on-line resistance probe sensor, as well as estimated by solution analysis of dissolved copper and standard weight loss measurements.

It was found that at room temperature, corrosion of the copper as indicated by an increase of the resistance of the probe is detected during the first 3-4 days of exposure. Subsequently, the corrosion potential reaches the immunity region of Cu as predicted by the relevant Pourbaix diagram. Accordingly, a decrease in the resistance of the on-line 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 (oxygen level < 0.001 ppb) established in the experiments. The average corrosion rate measured from weight-loss and solution analysis basically represents the transient phase of the experiment, as shown by a comparison between the different methods of corrosion rate measurement. 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.

**Keywords:** copper, general corrosion rate, anoxic groundwater, online resistance probe sensor, solution analysis

# KUPARIN KORROOSIO HAPETTOMASSA 1 M NaCl –LIUKSESSA

## TIIVISTELMÄ

Tässä työssä tutkittiin kuparin käyttäytymistä 1 M NaCl - liuoksessa sekä huoneen että 80 °C:n lämpötilassa lähes hapettomissa olosuhteissa, joissa arvioitu liuenneen hapen määrä oli 0.001-0.01 ppb. Korroosion määrää enimmillään 30 vuorokauden altistuskokeissa seurattiin kolmella eri tavalla: on-line-vastuslanka-anturilla, liuenneen kuparin määrän perusteella ja standardipainohäviömittausten perusteella.

Huoneen lämpötilassa kuparin korroosio eteni vastuslanka-anturin näyttämään perustuen ensimmäisten 3-4 altistuspäivän aikana. Tämän jälkeen korroosiopotentiaali saavutti sellaisen Pourbaix-diagrammin mukaisen alueen, jossa kupari ei liukene ja korroosio ei etene. Vastuslanka-anturin vastus pienentyi jonkin verran johtuen todennäköisesti liuenneen kuparin uudelleen saostumisesta langan pintaan.

Kuparin korroosio huoneen lämpötilassa käytännöllisesti katsoen pysähtyy 60-80 tunnin jälkeen lähes hapettomissa olosuhteissa (liuenneen hapen määrä <0.001...0.01 ppb). Painohäviömittausten ja liuoksesta analysoidun liuenneen kuparin määrän perusteella laskettu korroosionopeus edustaa käytännössä vain alkuvaiheen transientin aikaista korroosiota. Tämä käy ilmi korroosionopeuden eri mittaustapojen tulosten vertailusta. Korroosio- ja redox-potentiaalin samankaltaisuus altistuksen aikana viittaa siihen, että ilmassa syntyneen oksidin liuetessa ja/tai yhdenarvoisen kuparin homogeenisessa hapettumisessa syntynyt kahdenarvoinen kupari toimii redox-potentiaalia määräävänä tekijänä suljetussa systeemissä.

**Avainsanat:** kupari, yleinen korroosio, anaerobinen pohjavesi, online- vastuslanka-anturi, liuosanalyysi

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## 1 INTRODUCTION

In the present KBS-3 design, spent nuclear fuel is planned to be packed in a canister made of graphite cast iron. The cast iron canister has an outer shield made of copper, which is responsible for the corrosion protection of the inner canister. The thickness of the wall of the copper canister is 50 mm, and this sets a limit of  $0.5 \mu\text{m y}^{-1}$  for the maximum corrosion allowance of copper for a predefined lifetime of 100 000 years.

General corrosion of copper may occur in deep repository conditions. For instance, it has been recently proposed on the basis of thermodynamic calculations (Beverkog & Puigdomenech, 1998) that there is a possibility of copper corrosion in highly saline water environments of the anoxic type (concentration of oxygen less than  $10^{-6} \text{ mol l}^{-1}$  (Vuorinen & Snellman, 1998)). In accordance to such predictions, corrosion rates several times higher than  $0.5 \mu\text{m y}^{-1}$  were measured for copper in saline groundwater in short-term experiments (Laitinen et al. 2001, Betova et al. 2003). In addition, long-term field experiments (Rosborg et al. 2001) have also indicated unacceptably high corrosion rates of copper in deep repository conditions. Accordingly, either experimental or theoretical results should show that the rate of general corrosion is acceptably low to prove the suitability of copper as a shield material.

In that connection, 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 corrosion sensor based on the measurement of the resistance of a copper wire probe, weight loss coupons and solution analysis. The goals of this study were to investigate to what extent pure copper will corrode in 1 M NaCl solution without the presence of oxygen. A secondary goal was 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 very low.

## 2 METHODS

Six copper specimens (weight loss coupons, Cu OFP, surface area 14 cm<sup>2</sup> each) were placed in an autoclave made of titanium (Ti) and titanium alloy (Ti-6Al-4V). In addition, a wire resistance probe sensor made of pure Cu (99.95%, Goodfellow, diameter 0.125 mm) was installed in the autoclave to monitor the corrosion rate online. The composition of both copper materials is given in Table 1.

**Table 1.** Composition (in ppm) of the test materials. NA - not analysed.

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

Dissolved oxygen was removed by nitrogen bubbling typically for 4-6 hours after the installation of the copper test specimens and the solution into the autoclave. No pre-flushing of the solution with N<sub>2</sub> prior to addition into the autoclave was used. The nitrogen gas was purified from oxygen using Oxisorb R 200 nitrogen purification system, which guarantees that the oxygen content of the nitrogen gas after the cleaning operation is less than 5 ppb. The electrolyte used was 1 M NaCl, the temperature was 23±1 °C or 80 °C and the pressure 1 or 14 MPa. The volume of the solution was 5 L at 80 °C and 2.5 L at 23 °C.

If oxygen removal is performed with 5.0 N nitrogen, which contains a maximum of 3 ppm (typically 1...2 ppm) oxygen as impurity, this should theoretically, after thorough flushing for a long enough time (4-6 hours), result in about 10 ppb O<sub>2</sub> in water (with a certain amount of oxygen left on the autoclave and specimen surfaces). According to the specifications of the Oxisorb R 200 nitrogen purification system, the starting O<sub>2</sub> content down to less than 5 ppb. Assuming the same distribution coefficient and effect of temperature we should have less than 0.02 ppb in the water on average. However, it has been reported (King et al. 2001) that the residual oxygen is always somewhat higher than that which would have been predicted based on a residual [O<sub>2</sub>] calculated from Henry's law.

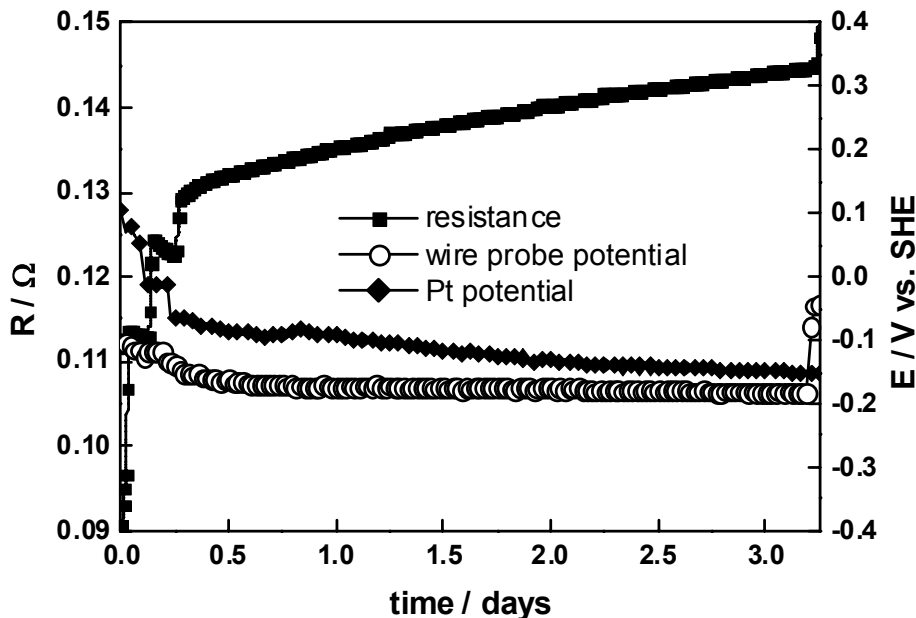
The redox-potential can in principle be used as a measure of the remaining dissolved oxygen content. A Pt electrode will respond as a redox electrode in the solution (since the [Cl<sup>-</sup>] is not sufficiently high to support extensive dissolution of Pt in the form of Pt-Cl<sup>-</sup> complexes), determined by the balance of the kinetics of the oxidation of various reduced species in solution and the reduction of the oxidants. However, at potentials approaching the hydrogen/water equilibrium, the influence of oxidising species other than water and oxygen has likely to be taken into account.

### 3 RESULTS

#### 3.1 6-day tests at 80 °C

The first test (test Nr 1) was performed using 99.999% N<sub>2</sub> gas (having 1...3 ppm of oxygen as impurity) without the Oxisorb oxygen scavenger system. Thus, the presumed dissolved oxygen content was 10 ppb. The Cu-flag electrode was constructed as a wire resistance probe so as to be able to follow on-line the corrosion rate of Cu as well as to follow the Cu corrosion potential. The results are shown in Figure 1 (on-line results) and Figure 2 (solution analyses for dissolved Cu).

The resistance of the Cu-flag electrode (resistance wire probe) increased very rapidly during the initial oxidic period (about two hours) and continued to increase more slowly for the rest of the test time (only the first 3.5 days are shown as the Cu-flag electrode wire was cut by corrosion at about  $t = 77$  hrs). The corrosion rate is estimated to be higher than  $100 \mu\text{m d}^{-1}$  in the first stage and  $1.5 \mu\text{m d}^{-1}$  in the latter stage. The increase from about 0.11 to 0.13  $\Omega$  is caused by the increase in temperature from RT (where the oxygen removal was performed for two hours) 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 pH (measured from ex situ samples) of the solution was in the beginning 6.4 and at the end 9.9. The solution analyses showed that the dissolved Cu varied between 800 and 1500  $\mu\text{g/l}$ , indicating deposition of Cu onto the autoclave walls. Thus the instantaneous corrosion rates estimated from the resistance probe measurements could be affected by Cu deposition on the wire probe. The variation of the dissolved Cu concentration with exposure time indicates also the possibility of electrolyte stratification due to the fact that no stirring of the solution was performed.



**Figure 1.** The redox (Pt) potential, the Cu-flag electrode potential and the resistance of the Cu-flag electrode as a function of time for test Nr 1 (without Oxisorb).

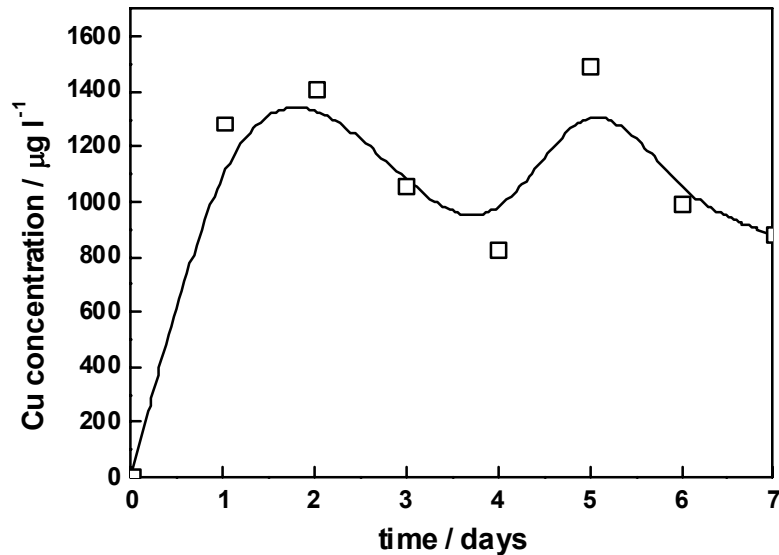


The corrosion coupons showed a total weight loss of 59.4 mg. The average general corrosion rate was estimated using the formula

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

where  $\Delta m$  = weight loss [g],  $\rho$  = density [ $\text{g}/\text{cm}^3$ ],  $A$  = surface area [ $\text{cm}^2$ ] ( $= n \cdot 14 \text{ cm}^2$ ,  $n$  = number of coupons) and  $t$  = exposure time [days]. The density of copper is  $8.94 \text{ g}/\text{cm}^3$ . A value of  $48 \text{ } \mu\text{m} \text{ y}^{-1}$  is obtained for the average corrosion rate.

The second test (test Nr 2) was performed otherwise similarly but with the Oxisorb - system, so that the gas arriving at the autoclave had less than 5 ppb of oxygen as impurity (according to the system specifications), which theoretically should result in having less than 0.01 ppb in the liquid phase. The on-line results are shown in Figure 3. Again, during the initial oxic period the resistance increased indicating very rapid corrosion. After oxygen removal the resistance was almost levelled off.

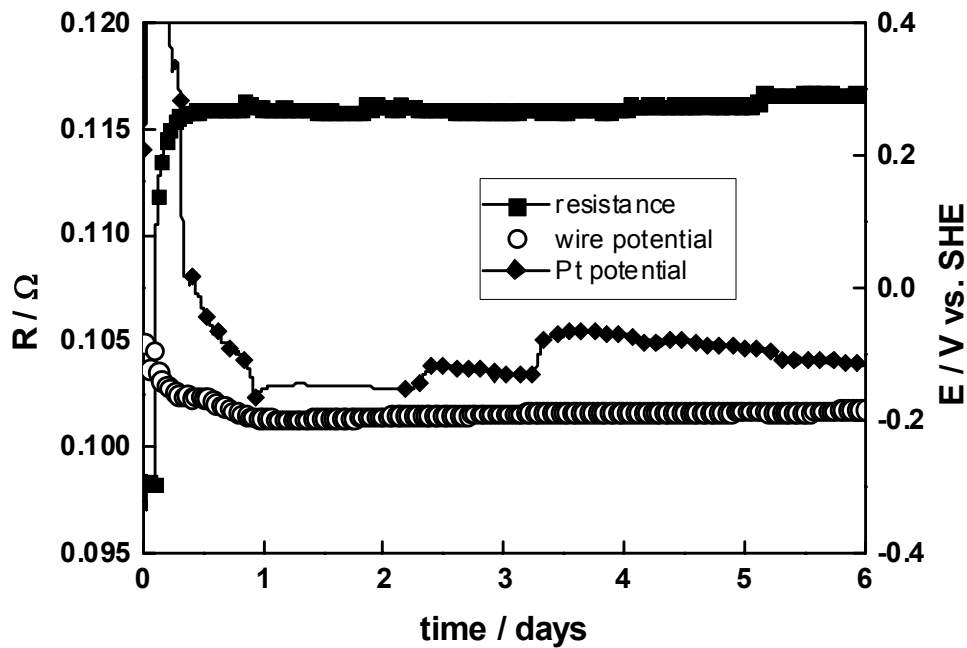


**Figure 2.** The solution analyses for dissolved copper during test Nr 1 (without Oxisorb).

The time variation of the depth of corrosion penetration,  $d_{\text{corr}}(t)$ , can be calculated by the formula (Ueno et al. 2003)

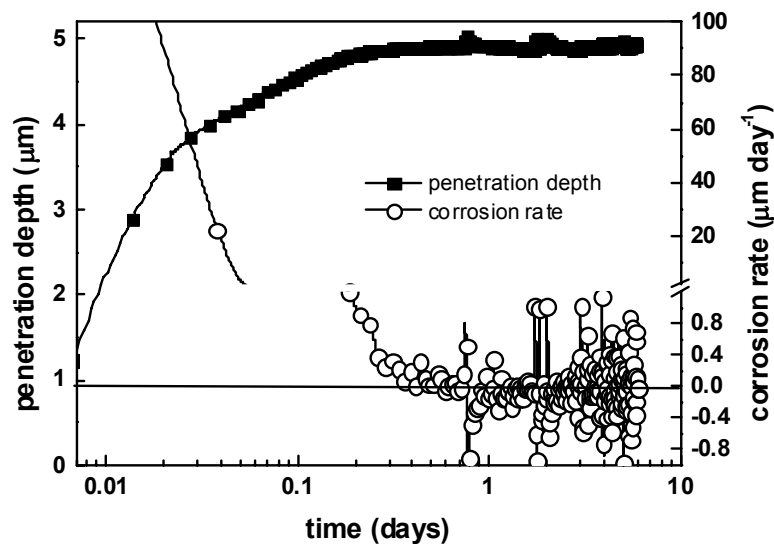
$$d_{\text{corr}}(t) = r_0 \left( 1 - \sqrt{\frac{R_0}{R(t)}} \right) [\mu\text{m}]$$

where  $r_0$  is the initial radius (= xx ) of the resistance probe,  $R_0$  the initial resistance value (= xx) and  $R(t)$  is the resistance value at a certain time of exposure( $t$ ).



**Figure 3.** The redox (Pt) potential, the Cu-flag electrode potential and the resistance of the Cu-flag electrode as a function of time for test Nr 2 (with Oxisorb).

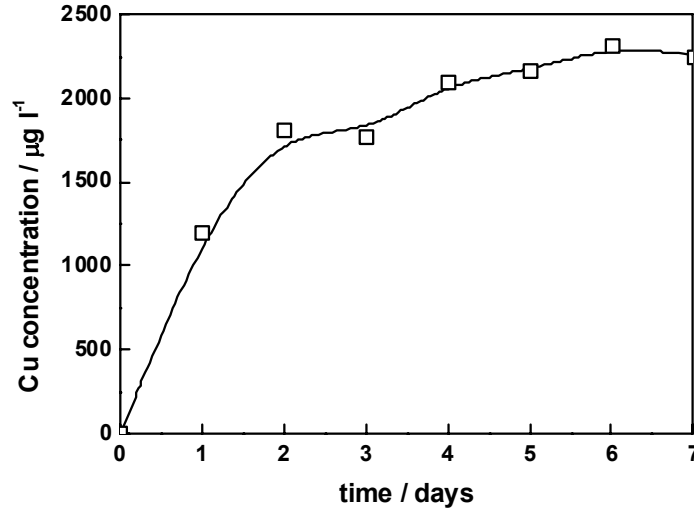
Such data are presented in Figure 4 with a logarithmic time scale to emphasise the initial period of exposure. The instantaneous corrosion rate, determined by numerical differentiation of the  $d_{\text{corr}}(t)$  curve after polynomial interpolation, is also shown in the Figure.



**Figure 4.** Depth of corrosion penetration (left ordinate) and differential corrosion rate (right ordinate) calculated from the resistance data for test Nr 2. Note the logarithmic time scale.

Three periods can be identified in Figure 4 - an initial period (0.5 h) with very rapid 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. However, at the same time the corrosion potential of Cu stabilised at about  $-0.2 \text{ V}_{\text{SHE}}$ , which is only  $0.02 \text{ V}$  lower than without Oxisorb (Fig.3). 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.

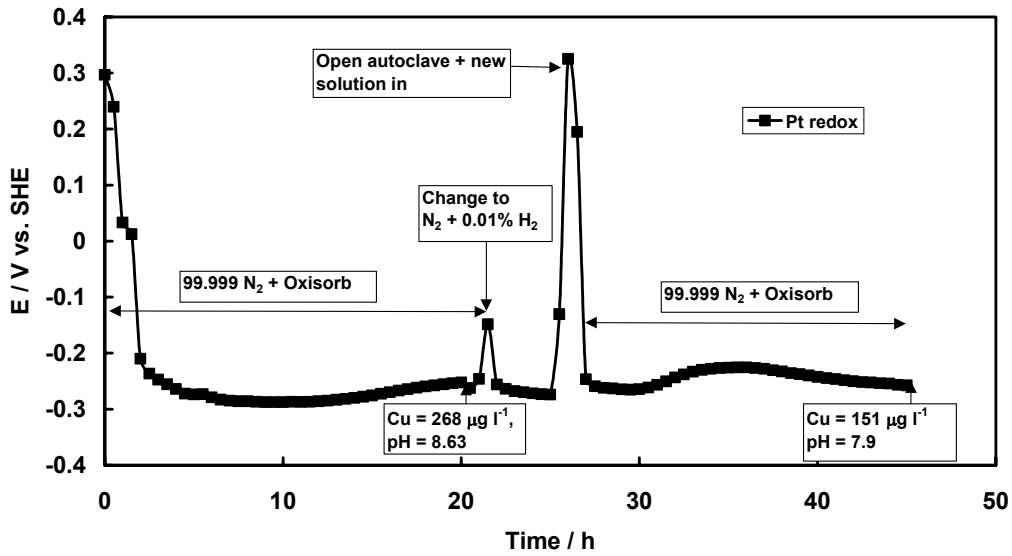


**Figure 5.** The solution analyses for dissolved Cu during the test Nr 2 (with Oxisorb).

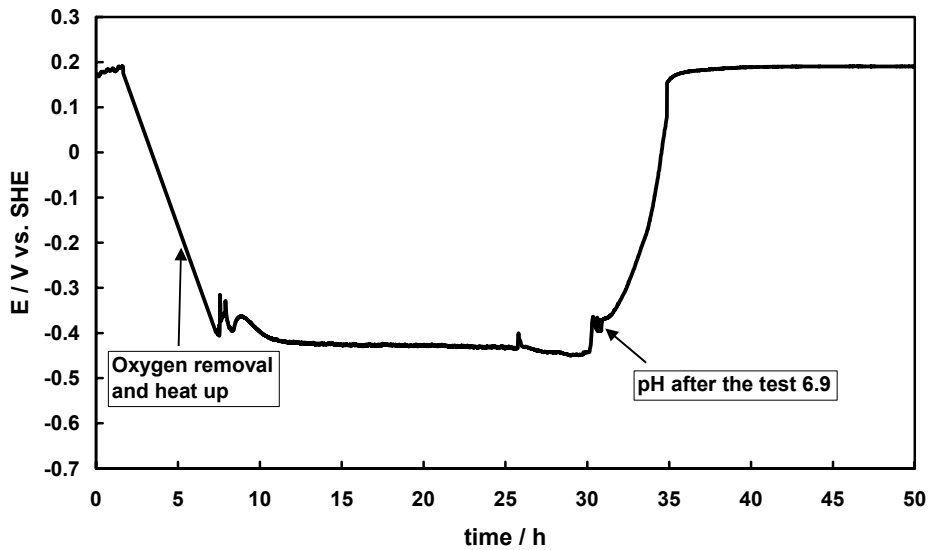
The solution analysis (Fig.5) showed an initial rapid increase of Cu to about  $1200 \mu\text{g/l}$  and a further slower increase to about  $2300 \mu\text{g/l}$ . The corrosion coupons showed a total weight loss of  $14.6 \text{ mg}$ , i.e. the average corrosion rate was  $11.8 \mu\text{m y}^{-1}$ .

The increase in pH during the tests is thought to be caused by the Cu corrosion reaction, where the cathodic reaction produces  $\text{OH}^-$  ions and the anodic reaction  $\text{CuCl}_2^-$  complexes. The  $\text{OH}^-$  ions accumulate in the electrolyte and produce the increase in pH. In the present case the total amount of corrosion in test Nr 1 was about  $60 \text{ mg}$ , which corresponds roughly to a  $2 \times 10^{-2} \text{ M}$  solution and an equivalent change in pH of about 2.3. In the test Nr 2 where the final pH was lower by about 0.4, also the total amount of Cu corrosion was lower by a factor of about 4. These findings tend to indicate that the presumption of the pH change being caused by corrosion of Cu is correct.

The rather high initial level of corrosion and the relatively high values of the redox-potential in the case of test Nr 2 could have indicated an oxygen leakage in the system which keeps the potentials high. To verify that a set of additional tests was performed. In these tests the same autoclave was used with the same Oxisorb oxygen removal system and the same Pt- electrode to measure redox-potential but with no Cu-specimens. It was considered that some Cu probably would still be present in the solution (dissolving from the autoclave walls where it was deposited during the two 6-day experiments). Figure 6 shows the redox-potential for these two tests. The redox potential varied between  $-0.29$  and  $-0.25 \text{ V}_{\text{SHE}}$  in the first test run and between  $-0.27$  and  $-0.23 \text{ V}_{\text{SHE}}$  in the second test run. These values are about  $0.1 \text{ V}$  to  $0.15 \text{ V}$  lower than in the two 6-day tests. At the end of the first test run the pressurizing gas was switched to  $\text{N}_2 + 0.01\% \text{ H}_2$ . This had no marked effect on the potentials. The solution analysis showed that in the first test run there was  $\text{Cu} = 268 \mu\text{g/l}$  (with end pH of 8.63) and in the latter test run  $\text{Cu} = 151 \mu\text{g/l}$  (with end pH of 7.9).



**Figure 6.** Potential of Pt-electrode (redox - potential) in two consecutive test runs without having the Cu-coupons in the electrolyte.



**Figure 7.** The Pt-potential (redox-potential) in a test performed in pure water at 80 °C and 14 MPa.

The system was further tested by changing the solution to distilled water and measuring the Pt redox-potential both at room temperature and at 80 °C (Fig. 7). Oxygen was removed from the solution by purging with 99.999% N<sub>2</sub> gas filtrated by the Oxisorb system. The redox-potential was about -0.44 V<sub>SHE</sub> at 80 °C (with pH after the test being 6.9). This test shows that in a solution which does not extensively dissolve Cu, the redox-potential in the autoclave system does reach a rather low value. This value can be used to estimate the dissolved oxygen content presuming that in this case dissolved oxygen is controlling the redox-potential and assuming that in the 6-day test Nr 1 the dissolved oxygen content was about 10 ppb. At 80 °C a ten-fold decrease in oxygen

content would be expected to result in a decrease of the redox-potential by 0.07 V. Thus, the decrease from about -0.15 V to -0.44 V, i.e. 0.29 V corresponds to a decrease in dissolved oxygen content down to about  $10^{-3}$  ppb. It was assumed in beforehand that the dissolved oxygen content after taking the Oxisorb system in use would be 0.02 ppb, so in this case some oxygen is also consumed in reactions with the autoclave walls.

In order to exclude the influence of the autoclave walls on the mass balance of Cu, further exposure tests were carried out in a glass vessel inserted in the autoclave at room temperature and normal pressure. These tests are described in detail below.

## 3.2 Tests at room temperature

### 3.2.1 Test procedure

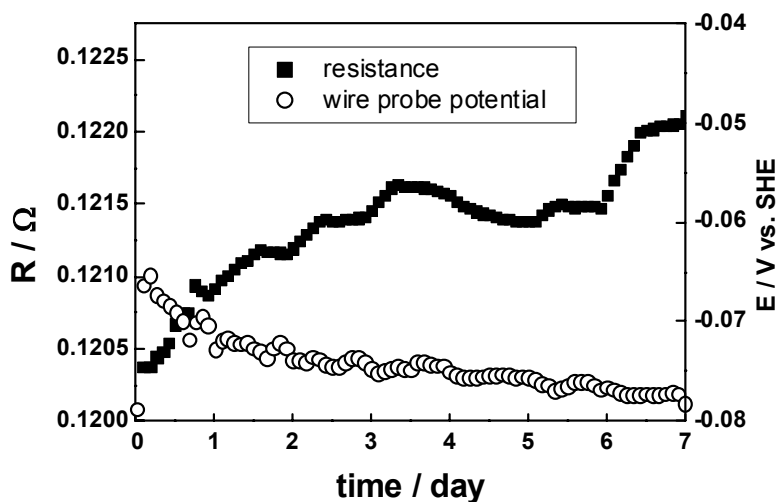
A test was performed at room temperature in a Pyrex glass vessel filled with 2.5 litres of 1 M NaCl installed inside the autoclave. The autoclave lid with a copper flag electrode, three Cu-coupons (about  $14 \text{ cm}^2$  exposed area each, connected with a lacquer-covered wire leading out of the autoclave through a wire feed-through), a Pt-electrode and a reference electrode were installed so that all the electrodes were immersed into the 1M NaCl solution. The Cu-coupons and the Cu flag electrode (Cu-wire probe, exposed length 4.5 cm) were cathodically protected via a potentiostat so that no corrosion was expected to take place during the initial oxic period.

The gas environment in the autoclave was made anoxic by replacing the initial gas with 5.0 N<sub>2</sub> gas which was further purified with Oxisorb R 200 system ( $C_{O_2}(\text{gas}) < 5 \text{ ppb}$ ). After purging the autoclave for 12 hours with 1 MPa overpressure the purging was stopped, the valves closed and the cathodic polarisation stopped. The test was then continued for 172 hours (ca. 7 days). At the end of the test a gas sample was taken from the gas volume and analysed for H<sub>2</sub>. After opening up the autoclave a sample was taken from the solution and analysed for dissolved Cu, the Pt-electrode was soaked in nitric acid to dissolve any deposited Cu and the nitric acid was analysed for Cu, and finally the Cu-coupons (with the lacquer-covered wire for cathodic polarisation purposes) were weighed for weight loss.

### 3.2.2 Results of the 6-day test

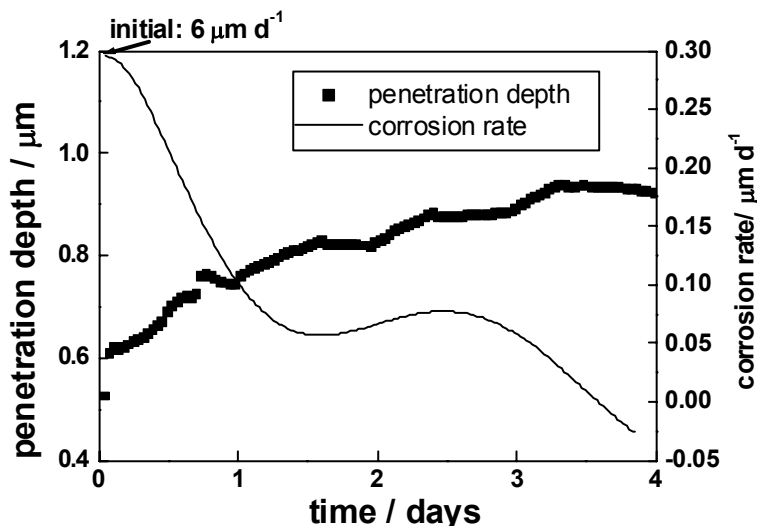
The gas sample was analysed with gas chromatography using a thermal conductivity detector. The analyses verified that the sample contained no hydrogen. The resolution limit of the technique used is 0.2 vol. % in the gas phase. It is however possible that the sensitivity of this technique used is not sufficient to unequivocally relate Cu corrosion to H<sub>2</sub> production. The sensitivity of the analysis could be increased by decreasing the headspace volume, decreasing the initial pressure of N<sub>2</sub>, and/or by increasing the length of the experiment.

Figure 8 shows the resistance and the potential of the Cu-wire electrode during the exposure in 1M NaCl at room temperature. The resistance increased slightly in the beginning (first 60 hours), stabilised after that but showed some small further increase at the end of the exposure. The potential of the Cu-wire electrode was about  $-0.065 \text{ V}_{\text{SHE}}$  at the beginning and decreased to  $-0.08 \text{ V}_{\text{SHE}}$  at the end of the test.



**Figure 8.** The resistance and the potential of the Cu-wire probe as a function of the exposure time during the 6-day test. Glass vessel, 1 M NaCl, room temperature, 1 MPa  $N_2$  (<5 ppb  $O_2$ ) overpressure, initial value of resistance 0.118  $\Omega$ .

Figure 9 shows the evolution of the corrosion depth as a function of time during the first 4 days of the test (when the increase of the resistance was observed; in Figure 8). The differential corrosion rate determined by numerical differentiation of the  $d_{\text{corr}}(t)$  curve after polynomial interpolation, is also shown in the Figure. Since such a procedure was found to be inadequate for the first 2 h of exposure, the initial differential corrosion rate was calculated by linear interpolation and indicated in the figure with an arrow. It can be concluded that the corrosion rate during the initial period is still rather high and it remains quite elevated up to ca. 3.5 days of exposure after which it drops essentially to zero.



**Figure 9.** Total corrosion depth,  $\mu\text{m}$  (left ordinate) and corrosion rate,  $\mu\text{m d}^{-1}$  (right ordinate) during the first 4 days of the 6-day test. The corrosion rate during the initial period of exposure is indicated by an arrow.

The three weight loss coupons showed a total loss of weight of 4.6 mg with a total surface area of 42 cm<sup>2</sup>. The calculated corrosion rate is 0.0074 mm/y, i.e. 7.4 µm/y. This corrosion rate is clearly higher than the allowed average corrosion rate of 0.5 µm/y.

The solution analyses from the glass vessel showed 460 µg/l of Cu, i.e. the total amount of dissolved Cu is 1.15 mg. The total amount of Cu deposited on the Pt-electrode was found to be 0.0815 mg. Comparing the total amount of Cu in the solution plus that found on Pt-electrode (i.e. 1.15 mg + 0.0815 mg = 1.23 mg) with that dissolved from the coupons (4.6 mg plus the 0.087 mg dissolved from the Cu-wire probe) indicates that a large amount of Cu must have deposited on the walls of the glass vessel. To verify that most of the electrolyte was removed from the glass vessel, the vessel was rinsed with 65% HNO<sub>3</sub> and the resulting solution was taken for solution analyses for Cu. A total amount of 2.93 mg Cu was determined. The accuracy of the solution analysis is about 30 µg/l or 0.08 mg for 2.5 litres of solution.

Summarising, the mass balance of Cu in the glass vessel can be written as

$$m_{\text{Cu}}(\text{solution analysis}) = m_{\text{solution}} [(1.15 \pm 0.08) \text{ mg}] + m_{\text{Pt counter}} [0.0815 \pm 0.0006] \text{ mg} \\ + m_{\text{glass walls}} [2.93 \pm 0.08] \text{ mg} = \mathbf{4.16 \pm 0.17 \text{ mg}}$$

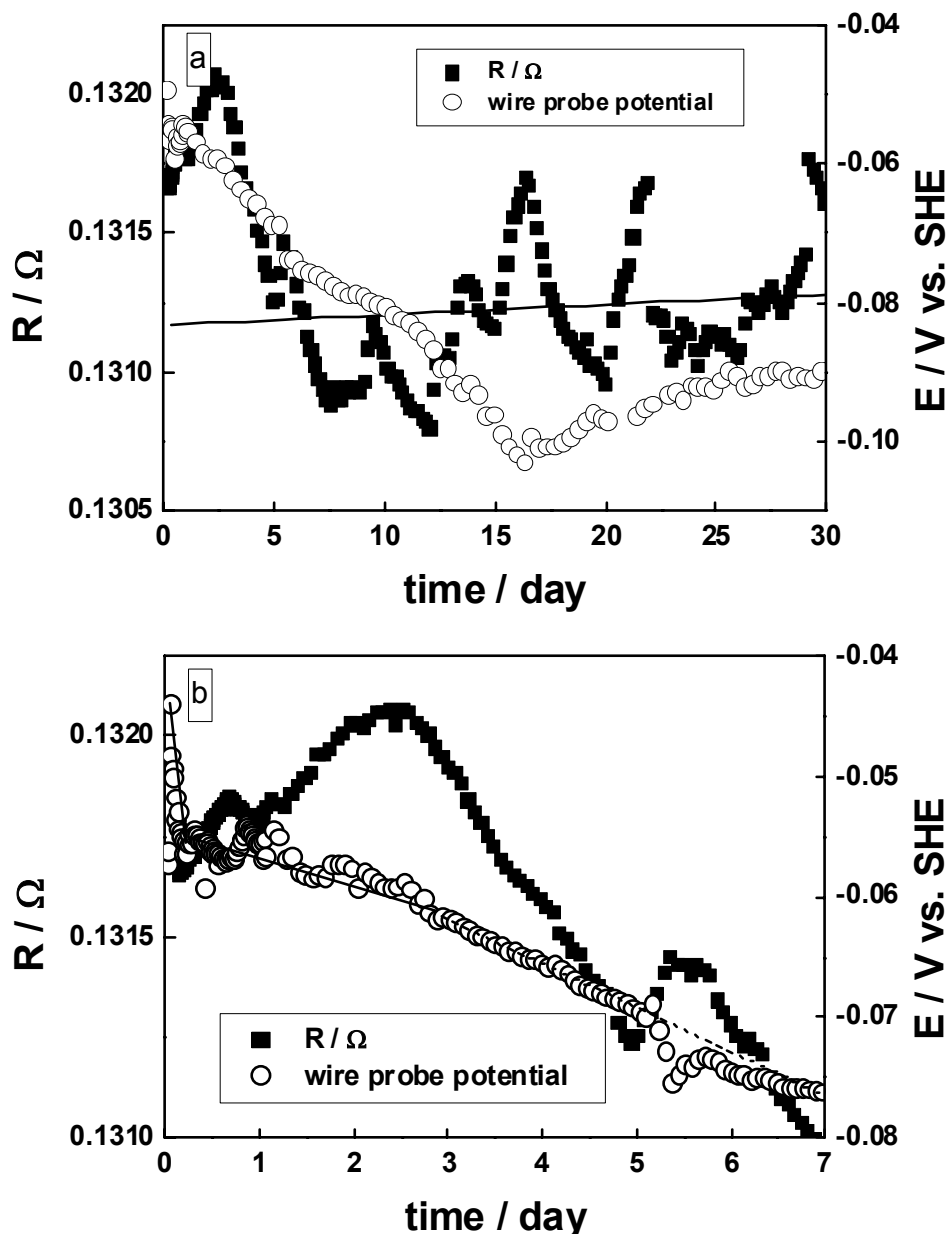
$$m_{\text{Cu}}(\text{weight loss}) = \mathbf{4.69 \pm 0.1 \text{ mg}}$$

The two values agree reasonably, i.e. we can conclude that the amount of corroded copper has been quantified using both methods.

### 3.2.3 Results of the 30-day test

As demonstrated above, no steady state condition was reached in the 6-day test performed at room temperature in 1 M NaCl. Further, the redox conditions during the 6-day test were not monitored. Thus a 30-day test was carried out in which the conditions described in paragraph 3.2.1 were maintained. An additional Pt electrode was installed in the autoclave and immersed in the glass vessel in order to measure the redox potential. Moreover, aliquot samples of the electrolyte were taken at the 2nd, 5th, 9th, 16th, 23rd and 30th day of exposure and analysed for dissolved copper. It is worth mentioning that the analysis of the gas phase for hydrogen could not be performed in this case because of a failure in taking the gas sample at the end of the test.

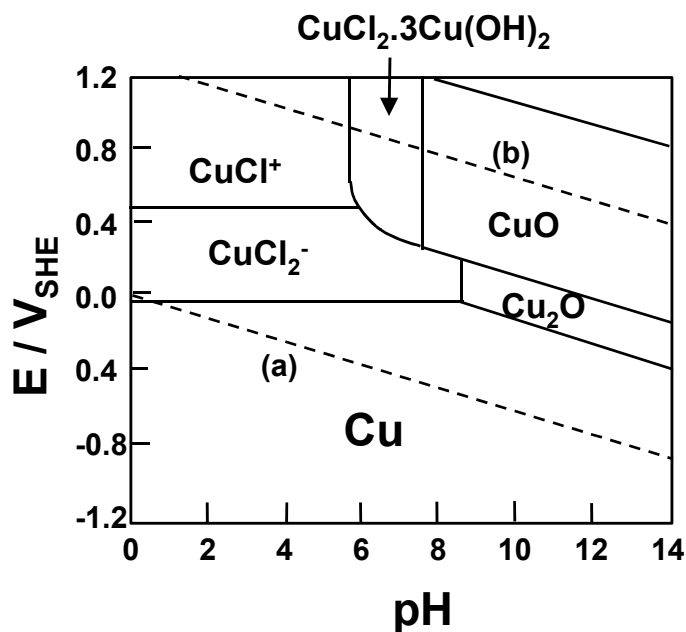
Figure 10a shows the evolution of the resistance and the potential of the Cu-wire probe as a function of time during the 30-day test, whereas Figure 10b presents a blow-up of the first 7 days of the test allowing the comparison with Figure 8.



**Figure 10.** (a) The resistance and the potential of the Cu-wire probe as a function of the exposure time during the 30-day test. Initial value of resistance 0.125  $\Omega$ , glass vessel, 1 M NaCl, room temperature, 1 MPa  $N_2$  (<5 ppb  $O_2$ ) overpressure. (b) blow-up of the first 7 days of the test.

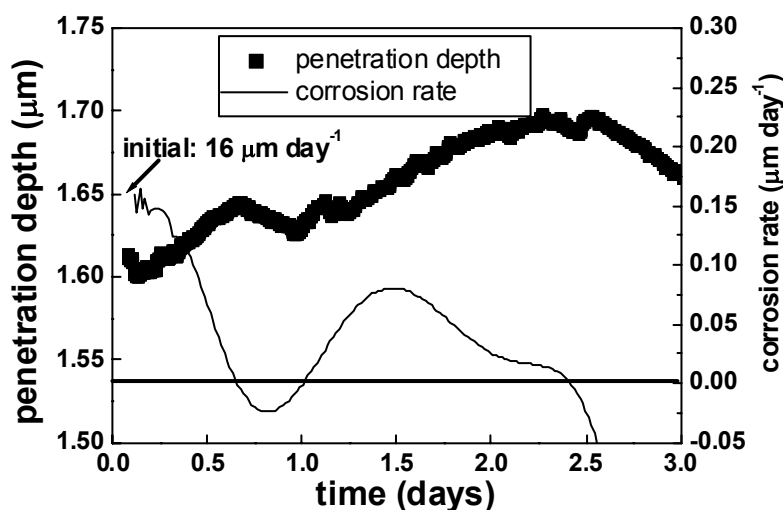
The comparison between Figure 8 and Figure 10b leads to the suggestion that the behaviour of copper during both tests is broadly similar. In other words, an initial very rapid increase of the resistance (not shown in the figures) gradually levels off, and a maximum in the resistance is reached after roughly 2.5-3.5 days of exposure. After that the resistance decreases indicating probably a deposition process. A closer look to Figure 10a shows that this behaviour is cyclic and the mean value of the resistance is practically similar between the 7th and 30th day of exposure indicating 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.





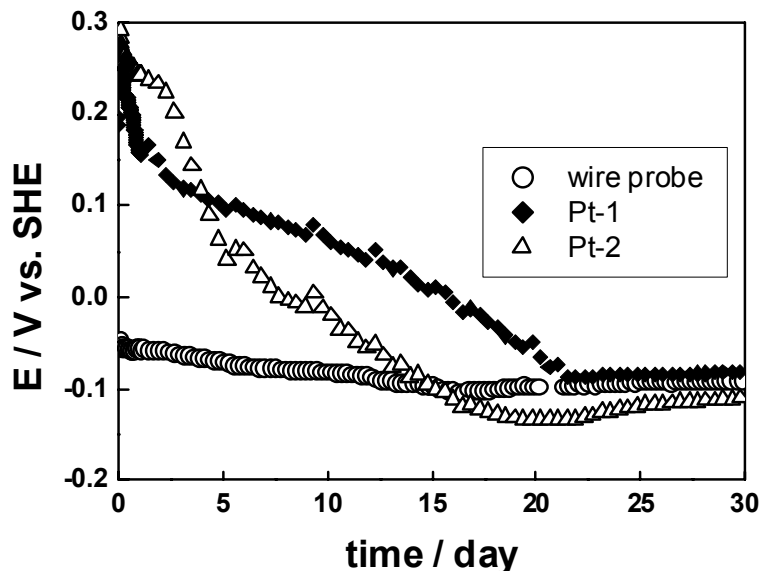
**Figure 11.** Pourbaix diagram for the  $\text{Cu} / \text{H}_2\text{O}$ ,  $1 \text{ M Cl}$  system at  $25 \text{ }^\circ\text{C}$  and activity of dissolved  $\text{Cu}$   $10^{-6} \text{ mol dm}^{-3}$  (King et al. 2001).

At the same time, the potential of the wire probe decreases as a function of exposure reaching a value of  $-0.1 \text{ V}$  vs. SHE after ca. 15 days of exposure (Fig.10a). This potential lies in the immunity region of  $\text{Cu}$  in  $1 \text{ M NaCl}$  at room temperature (King et al. 2001) according to the relevant Pourbaix diagram shown in Figure 11. Figure 10b demonstrates that the different stages in the decrease of the copper wire potential (marked with black lines) correlate to a certain extent with the behaviour of the resistance, i.e. during corrosion (increase of the resistance with time) the slope of the potential vs. time curve differs from that during deposition (decrease of the resistance with time).

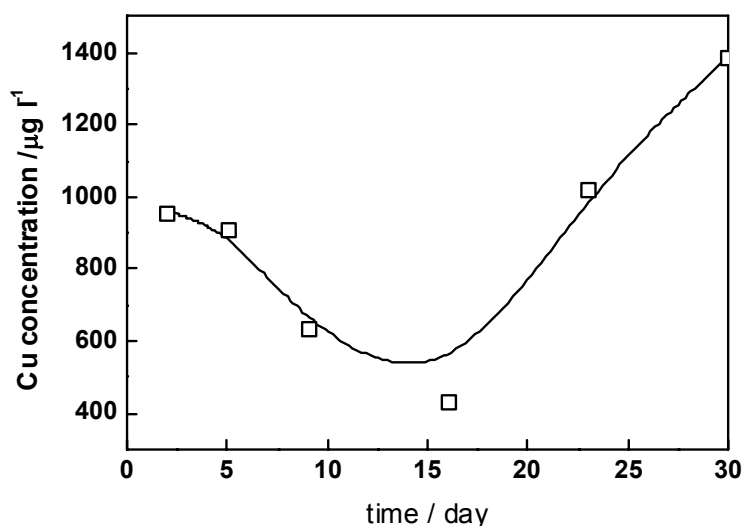


**Figure 12.** Total corrosion depth,  $\mu\text{m}$  (left ordinate) and corrosion rate,  $\mu\text{m d}^{-1}$  (right ordinate) during the first 3 days of the 30-day test. The corrosion rate during the initial period of exposure is indicated by an arrow.

Figure 12 shows the evolution of the corrosion depth as a function of the exposing time during the first 3 days of the 30-day test. The differential corrosion rate is also shown in the Figure. It can be concluded that in analogy to the 6-day test (Fig. 8), the corrosion rate during the initial period is very high, decreasing essentially to zero after 2.5 days of exposure.



**Figure 13.** The potential of the Cu-wire probe and the potentials of the two Pt electrodes vs. time during the 30-day test. Glass vessel, 1 M NaCl, room temperature, 1 MPa  $N_2$  (<5 ppb  $O_2$ ) overpressure.



**Figure 14.** Copper concentration in the electrolyte during the 30-day test in 1 M NaCl.

Figure 13 compares the potential of the Cu-wire probe with those of the Pt flag electrode (Pt-1) and the Pt-counter electrode (Pt-2) after the cathodic polarisation of the copper samples was switched off. The evolution of the potentials of the two Pt electrodes as a function of exposure is broadly similar, bearing in mind the fact that Pt-2 was polarised for ca.12 h in the oxygen evolution region (it was used as a counter

electrode during the cathodic polarisation of the Cu samples). That is, an initial fast decrease is followed by a slower one and finally the potentials reach values close to each other and to that of the Cu wire probe ( $-0.1 \pm 0.02$  V vs. SHE).

Figure 14 shows the results of the solution analysis for copper during the 30-day test. A high concentration of Cu (ca.  $1 \text{ mg l}^{-1}$ ) is found already after the 2nd day of exposure. A decrease in the copper concentration is observed between 5 and 16 days most probably due to electrolyte stratification (it has to be recalled that the experiments were performed in a quiescent solution). A value of  $1.39 \text{ mg l}^{-1}$  is reached after 30 days of exposure.

The total amount of Cu deposited on the two Pt electrodes determined by a procedure analogous to that described in paragraph 5.2.2 was found to be 0.225 mg. The analysis of the remaining solution in the glass vessel after the test showed 12.8 mg of Cu. It is to be recalled that the accuracy of the analysis is ca. 0.08 mg. Thus the total amount of dissolved Cu is estimated to be  $13.02 \pm 0.08$  mg. The total weight loss of Cu from the weight loss coupons was determined to be  $12.1 \pm 0.1$  mg. It can be concluded that a reasonable mass balance for Cu was reached also during the 30-day test. However, for a better account of the mass balance of Cu the reproducibility of the results has to be checked by repeating the tests, which has not been done in this study.

The average corrosion rate estimated from weight loss was  $3.9 \text{ } \mu\text{m y}^{-1}$ . This is still a too high value in comparison to the upper allowable limit of  $0.5 \text{ } \mu\text{m y}^{-1}$ . The depth penetration of corrosion in the wire probe reaches on the average  $1.5 \text{ } \mu\text{m}$  after 5 days of exposure and stabilises thereafter, indicating that the corrosion rate is practically zero after the initial period. Assuming that the total weight loss from the coupons has been obtained during the first 5 days of exposure, we estimate the penetration depth of corrosion as  $0.012 \text{ g} / 8.94 \text{ g cm}^{-3} / 42 \text{ cm}^2 \times 5 \text{ days} = 1.6 \text{ } \mu\text{m}$ , 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.

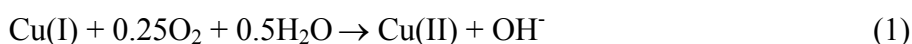
## 4 DISCUSSION

With the Oxisorb R 200 - system, the oxygen content in the 5.0 N<sub>2</sub> - gas is reduced to less than 5 ppb. When this gas is used to remove dissolved oxygen from electrolyte (in this case 1 M NaCl) theoretically we should arrive at a dissolved oxygen content of about 0.01 ppb. Based on the results from the test run in pure water without the Cu-specimens the dissolved oxygen content was estimated to be about 0.001 ppb at 80°C.

The results of the online monitoring of the copper corrosion with the wire probe sensor in both the 6-day and the 30-day tests demonstrate that the corrosion virtually stops after 2.5-3.5 days of exposure at room temperature. For longer times, a very slow oscillatory pattern of the penetration depth as a function of time is observed, the mean value being practically constant within the detection limit of the sensor. 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 remains quite close to -0.1 V vs. SHE, which can be explained by the fact that relatively large amounts of Cu are deposited on the Pt electrodes, making them to behave virtually as Cu electrodes.

The following qualitative hypothesis based on the large amount of kinetic data on the corrosion of Cu in chloride solutions (King et al. 2001) is proposed to explain the observed behaviour of Cu especially during the 30-day test.

When a Cu electrode is immersed in the 1 M NaCl solution, dissolution of the native oxide containing both monovalent and divalent copper proceeds and aqueous complexes of copper are formed. Due to the fact that a quiescent solution was used in the measurements, some Cu(II) is assumed not to be reduced back to copper metal, even though the dissolved oxygen content is very low and reduction is thermodynamically favoured. Alternatively, it can be proposed that the soluble Cu(I) is oxidised by the remaining oxygen in the solution to Cu(II) in a homogeneous reaction

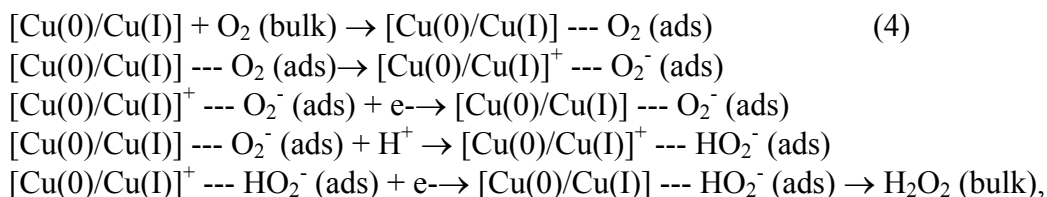


It is presumed that mainly the hydroxo-complexes of Cu(I) will oxidise to Cu(II), according to literature data (Sharma & Millero 1988, Plyasunova et al. 1997) showing that the stability of Cu(I) chlorocomplexes is much higher than that of the hydroxocomplexes and vice versa for Cu(II).

The divalent Cu can act as oxidant during corrosion of Cu



After the consumption of the most part of the oxygen, the potential of Cu will reach the immunity region. This causes the anodic reaction (2) to proceed in the reverse direction resulting in the deposition of metallic copper. As the reduction of oxygen on Cu has been proposed to follow the peroxide route on catalytic Cu(I) sites neighboured by Cu(0) (King et al. 1995):



after the consumption of the [Cu(0)/Cu(I)] sites during redeposition of Cu the oxygen reduction will be slowed down. The remaining very small quantities of oxygen will participate in reaction (1), thus re-initiating the cycle (1)-(3) until all the oxygen has been consumed. Due to the very low rate of reaction (1) in the high chloride- and very low oxygen- containing solution, the rate of reaction (3) will be very low, maintaining a very low corrosion rate for a relatively long period.

Alternatively, the observations be explained by the reaction of disproportionation of Cu(I)



The occurrence of such a reaction would explain the deposition of Cu on the glass vessel walls of the room-temperature test, whereas the presence of Cu(II) in solution would explain the relatively positive redox potentials observed in the presence of Cu. According to such a hypothesis, the presence of Cl<sup>-</sup> should inhibit the extent of disproportionation. Thus the hypothesis can be verified by repeating the experiments at various [Cl<sup>-</sup>].

## 5 CONCLUSIONS

The following main conclusions can be drawn from the results:

- Copper corrodes with an appreciable rate during the initial few hours of exposure to 1 M NaCl containing very small amounts of oxygen (ca. 0.01 ppb). Subsequently, the corrosion rate decreases, being however noticeable up to 3-4 days of exposure. For longer exposure times up to 30 days, the corrosion rate becomes negligible (close to zero) as oxygen level in the longer exposure time experiments is estimated to be < 0.001 ppb. Back deposition of copper has also been found to occur.
- 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 cannot be used to monitor reliably the redox potential because copper deposition on such electrodes transforms them into Cu-like electrodes. Thus the remaining oxygen in the system can only be estimated indirectly by monitoring the amount of copper corrosion. Such an estimate is however complicated by the participation of soluble Cu(II) formed by homogeneous oxidation or disproportionation of Cu(I) in the overall reaction on the copper surface.

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