



Hydrogen gas production during corrosion of copper by water

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ABSTRACT

This paper considers the corrosion of copper in water by: (1) short term, open system weight measurements and (2) long term, closed system immersion in distilled water (13,800 h) without O₂ at 21–55 °C. In the latter experiments, the hydrogen gas pressure is measured above the immersed copper and approaches $\sim 10^{-3}$ bar at equilibrium. This pressure is mostly due to copper corrosion and greatly exceeds that in ambient air. Accordingly, this measured hydrogen pressure from copper corrosion increases with temperature and has the same dependency as the concentration of OH⁻ in the ion product [OH⁻] [H⁺].

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1. Introduction

Due to the growth of visible reaction products the tarnish on copper-based materials needs to be removed in order to keep them shiny over the years. Most corrosion studies of copper have been performed in contact with air in our atmosphere. An exposure to hydrogen gas at atmospheric pressure is a well-known way to avoid tarnish on pure copper immersed in deionised liquid water and it is sometimes believed, but experimentally unsupported, that water itself will not corrode copper. This belief often comes from that hydrogen-free copper oxides can only exist near room-temperature below a certain hydrogen activity and it is assumed that this hydrogen activity is approximately the same as the hydrogen gas pressure. The hydrogen gas pressure in our atmosphere has been tabulated as 5×10^{-7} bar and is obviously far from atmospheric pressure. To understand the corrosion of copper in water we need to consider several issues including the activity of hydrogen gas and the operative reaction product. The main aim of this publication is to determine the pressure of hydrogen gas required to avoid tarnish of polycrystalline copper in liquid distilled water at different temperatures.

Results of hydrogen gas release from copper corrosion in distilled water were originally published 25 years ago in this journal [1] and followed up in recent publications [2,3]. We believe that knowledge of corrosion of copper as well as implications from various applications can be gained from the present study. For clarity we use the terms molecular hydrogen or hydrogen gas for H₂, the

word hydrogen for H and analogously for oxygen. Consequently, with these terms water contains both oxygen and hydrogen. Liquid water furthermore contains H⁺ and OH⁻ ions via partial dissociation (autoprotolysis) of the water molecule. Therefore liquid water facilitates the supply of a corrosion couple where CuH and CuOH are possible precursors or end products. This approach was taken thirty years ago in studies of water reactions on different crystallographic surfaces on metals with analysis techniques based on ultra high vacuum [4,5] and was later used in potential-pH diagrams [6].

Oxygen in the reaction product on copper also originates from water in a gas mixture with equal amounts of O₂ and H₂O but no attempt was made in that study to characterise the corrosion product [7]. It is generally observed that the 3-dimensional hydroxide Cu(OH)₂ is found and it is often believed that the mono-valent CuOH can only exist in 2-dimensional layers. However, we expect also CuOH to exist in 3-dimensional structures under certain conditions [3]. Obviously there is a need for an *in situ* method for characterisation of reaction products also in surfaces like grain-boundaries under relevant conditions. Such a characterisation is difficult, however, and not attempted here. To fulfil the main aim of this publication we discuss and interpret new detailed results of hydrogen gas detection in corrosion of Cu by liquid water at different temperatures. This hydrogen production takes place without any applied potential.

2. Experimental

In experiments described here, ≥ 99.95 wt%, OFHC-Cu with an as received surface finish has been used in hard or tempered con-

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dition in the form of 0.1 mm thick foils with average grain size of approximately 20 μm . Rods with 2 mm diameter of 99.995 wt%, OFHC-Cu ground to 1200 mesh with SiC paper have also been used in exposures of samples for 15 years in Fig. 7.

Fig. 1 shows a sketch of the experimental arrangement for quantitative detection, in the form of pressures of hydrogen gas in immersion of 140 cm^2 Cu. Apart from Cu, the closed system contained 0.1 mm thick, 17 mm diameter, >99 wt% palladium (Pd), 250 cm^2 stainless steel (SS) 316L in the ultra high vacuum system and 90 cm^3 of distilled water. Pd serves here as a membrane and separates hydrogen gas from water vapour [8]. The absolute pressure meter below the membrane is used for determination of temperature via the well-established influence of temperature on the water vapour pressure. This meter measures total pressure, but the contribution of H_2 to the total pressure is measured above the membrane. Therefore the meter below the membrane is suitable for temperature determination.

In the exposure with results presented in Figs. 4a and 4b dissolved air in the distilled water was in the start of the exposure removed by repeated evacuation 14 times of the gas phase volume above the liquid water [3]. A slight boiling of the water during the approximately 10 s evacuation increased the rate of gas removal. This procedure of evacuations took in all approximately 10 h.

Secondary ion mass spectrometry, SIMS, was used with a primary 4 keV Cs^- ion beam, and secondary ions from approximately 100 $\mu\text{m} \times 100 \mu\text{m}$ were detected with results shown in Figs. 6 and 7. In the short time exposure with NaOH addition to distilled water at room-temperature, the sample was carefully polished down to submicron flatness to optimize depth resolution of the formed reaction product in the subsequent SIMS analysis.

3. Background results

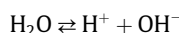
The corrosion rate can be found in weight loss measurements where the dissolution of the solid reaction product can be an approximate measure of corrosion of the metal. This takes place at a sufficient amount of water in the exposure of the metal where any suppression of corrosion rate, due to formation of a solid reaction product, is negligible.

Fig. 2 shows how the amount of water per time unit and Cu-surface influences the weight of Cu in water exposure. Obviously we can expect a weight gain or a weight loss depending on the access of water. This phenomenon is simply explained by one rate for

reaction product dissolution and another rate for formation of the reaction product. In atmospheric corrosion without any precipitation we expect a weight gain of Cu.

The influence of the concentration of protons on the corrosion rate of Cu is seen in Fig. 3. By necessity other ions apart from OH^- are needed for a variation of the concentration of protons. The variation of proton (H^+) concentration was obtained by additions of NaOH or HCl to 5 dm^3 distilled water. At room-temperature only a proton concentration of $10^{-7} \text{mol l}^{-1}$ water can be obtained without additions of other ions. We interpret the phenomenological role of proton concentration (pH) in Fig. 3 as:

- at high concentrations of protons, pH 0–4, protons will be consumed and replaced by positive Cu-containing ions;
- at medium concentrations of protons, pH 5–8, the supply of protons comes from partial dissociation of water:



- at low concentrations of protons, pH 13–14, the un-dissociated water molecules supply protons.

Bubbling of oxygen gas, shown in Fig. 3, has an effect on the corrosion rate of Cu only at high consumption rates of protons, which takes place at pH 2–4 in this figure. This bubbling can then be rate-determining for the corrosion rate. In Ref. [9], results are presented from dissociation measurements of molecular oxygen at $p_{\text{O}_2} = 20$ mbar on different materials and it is found that there is a huge variation of the dissociation ability among different materials and also the most well-known catalysts platinum and ruthenium dissociate O_2 far less than what is theoretically possible. Actually, on average only one in 10^{11} impinging O_2 -molecules on the surface dissociate to atomic oxygen ($\text{O}_2 \rightarrow 2\text{O}$) near room-temperature. Naturally, the rate of H_2 -dissociation also varies among different materials [10,11] although, to our knowledge, not many materials have been studied [12].

4. Present results and general discussion

4.1. Measurements of H_2

Air is initially removed in the studied system as described in reference [3]. The main aim here is to measure the H_2 -pressure from Cu corrosion in distilled water. Fig. 4a shows the detected H_2 -pressure from 4800 to 8800 h and Fig. 4b from 8800 to

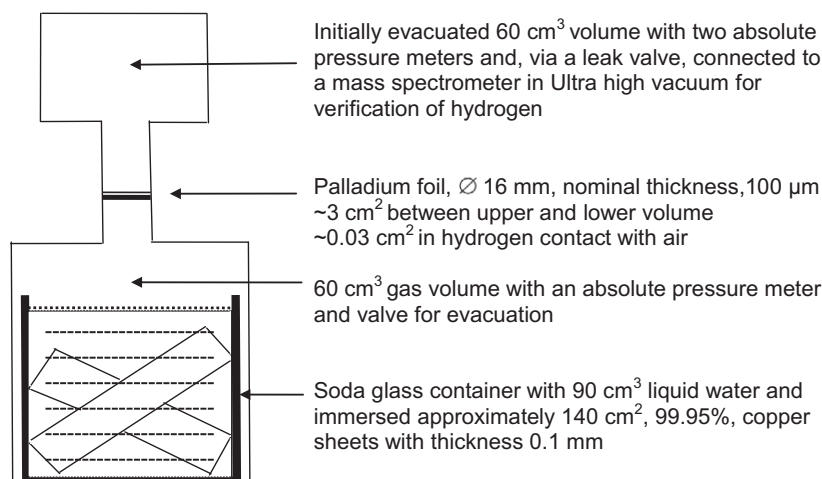


Fig. 1. Sketch of equipment used for studies of hydrogen evolution in Cu corrosion in distilled liquid water. Equipment of stainless steel 316L and ultra high vacuum gaskets of Cu with approximately 2 cm^2 area.

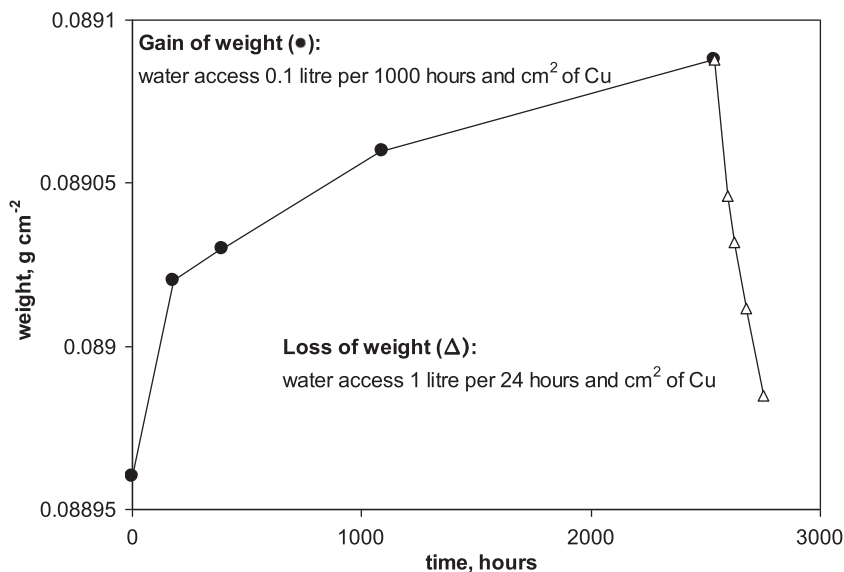


Fig. 2. Weight of 50 cm² Cu samples at two different accesses of water. pH approximately 7.

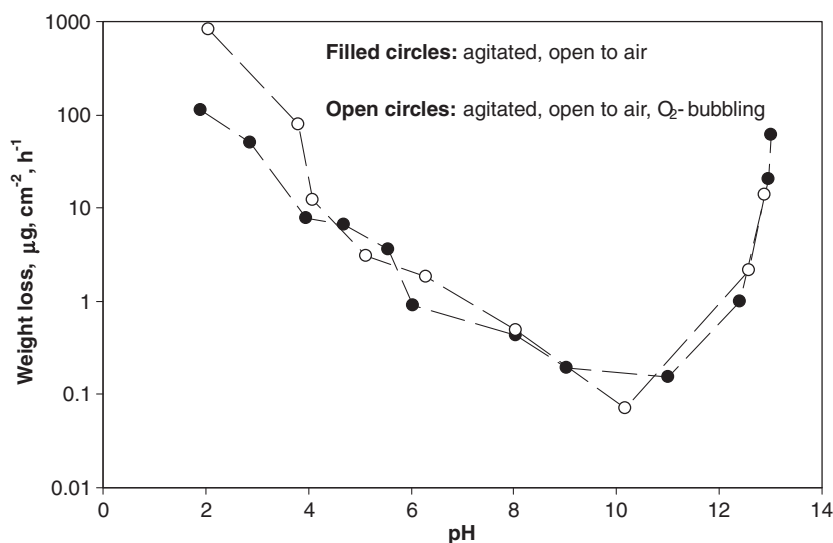


Fig. 3. Weight loss of Cu at different pH. Access of water: 1 l cm⁻² Cu per 24 h. This weight loss approximates Cu corrosion.

13,800 h. These figures show the effects on the measurements of varied temperature and also the effects of removal of hydrogen gas. In the detailed Figs. 4c–4h interpretation of the various effects is written in the respective graph. Upon a temperature change there is a more or less instantaneous hydrogen pressure change which is a consequence of a changed temperature of the closed system and therefore also in the gas above the Pd-membrane. It is also seen that both the Cu metal and the Pd membrane [8] influence the measured H₂-pressure but not at equilibrium (steady state). In these detailed graphs we can also estimate the diffusion coefficient of hydrogen from the relation

$$L = 2(Dt)^{1/2} \quad (1)$$

where L is diffusion length, D is diffusion coefficient and t is time. L is in this case the thickness of the immersed Cu samples, 0.1 mm, and t is 10–100 h, depending on temperature. The result of this estimate is a diffusion coefficient in the order of 10^{-13} – 10^{-12} m² s⁻¹.

Such a value is reasonable [13] but of course is expected to vary from grain-boundaries to grains of the Cu samples and therefore grain size.

The corrosion of Cu leads to the presence of molecular hydrogen in the gas phase but also hydrogen in the Cu substrate. A temperature decrease often also causes a hysteresis due to a slow reduction of the reaction product. Cu is then “supersaturated” with hydrogen at the lower temperature. In contrast to Cu there is more hydrogen in Pd at the lower temperature [8] and this can easily “shadow” hydrogen release from the corrosion of Cu. Since hydrogen is in different phases we should use a hydrogen activity which is the same in all phases at equilibrium/steady state of Cu corrosion (Figs. 4a–4h).

Fig. 5 is based on the measured hydrogen pressure close to equilibrium (steady state) in Cu corrosion from Figs. 4a and 4b (●). Experimental data in Fig. 5 are from 0.395 mbar, 21 °C at 12,600 h, 0.584 mbar, 30 °C at 10,700 h, 0.853 mbar, 40 °C at 9450 h, 1.009 mbar, 45 °C at 5100 h and 1.368 mbar, 55 °C at 7450 h. This

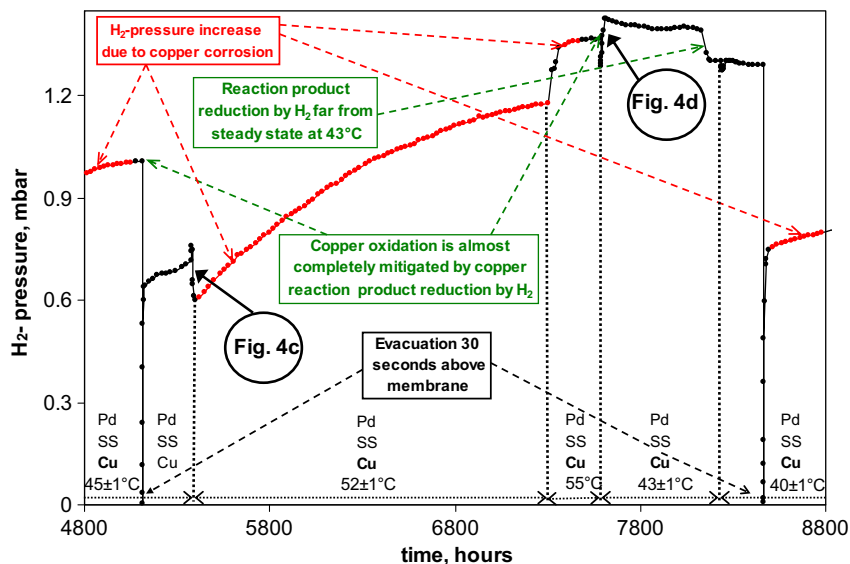


Fig. 4a. Measured H₂-pressure above membrane as a function of time in order to extract influence of temperature on corrosion of Cu in distilled water.

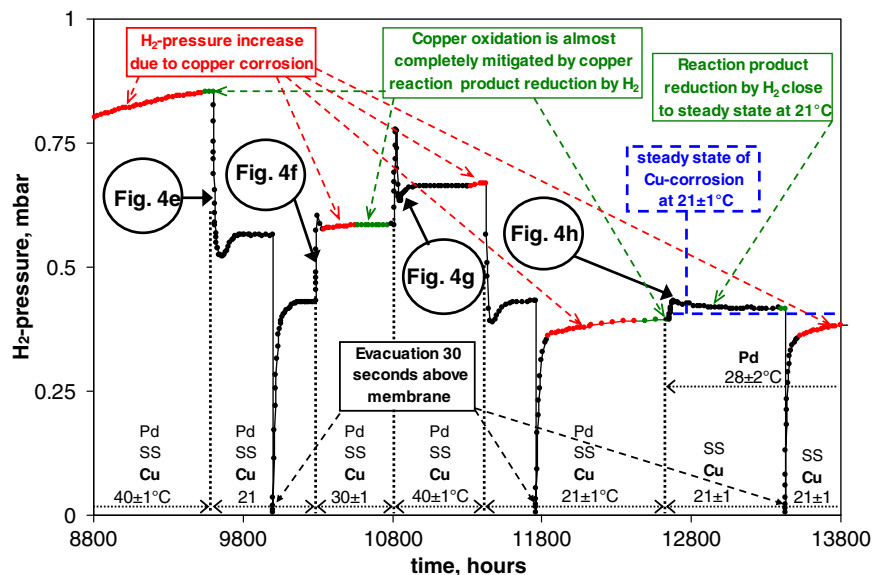


Fig. 4b. Measured H₂-pressure above membrane a function of time in order to extract influence of temperature on corrosion of copper in distilled water.

refers to H₂-pressures (steady state) directly after the relatively slow pressure increase to ensure that Cu is in equilibrium (near steady state) with respect to hydrogen activity in the system. These measured pressures are compared with well-established and tabulated influence of temperature on:

1. The presence of OH⁻ in distilled water (●)
2. Water vapour pressure (■)
3. Pressure of gases in a closed system (▲)

This comparison in Fig. 5 shows that the corrosion of Cu is mainly governed by the presence of the ion OH⁻ and not the vapour pressure of water which has a much stronger temperature dependence than the OH⁻-ion. For example, at 22 °C the water vapour pressure is 25 mbar and at 55 °C it is 157 mbar which means that it is more than a factor of 6 higher at the higher temperature whereas the measured equilibrium H₂-pressure is found to be only a factor of 3.5 higher at 55 °C relative to that at 21 °C. Actually, the

observed temperature influence rules out any significance of corrosion above the distilled liquid water.

Our results strongly indicate that water is consumed by copper via



where more OH⁻ is present upon a temperature rise of the distilled water. The variation of OH⁻ concentration at different temperatures is therefore a main reason for the temperature influence on corrosion of Cu in distilled water.

Our interpretation of corrosion of Cu in distilled liquid water in the absence of molecular oxygen is that Cu–H together with Cu–OH forms a corrosion couple where Cu–H bonds are involved and lead to hydrogen in the metal and molecular hydrogen, H₂, above the immersed Cu. The transport properties of molecular hydrogen and atomic hydrogen are relevant in this description. The dissociation rate of molecular hydrogen, giving atomic hydrogen, is a catalytic property of the reaction product. This dissociation of molecular hydrogen is a prerequisite for reduction of the reaction

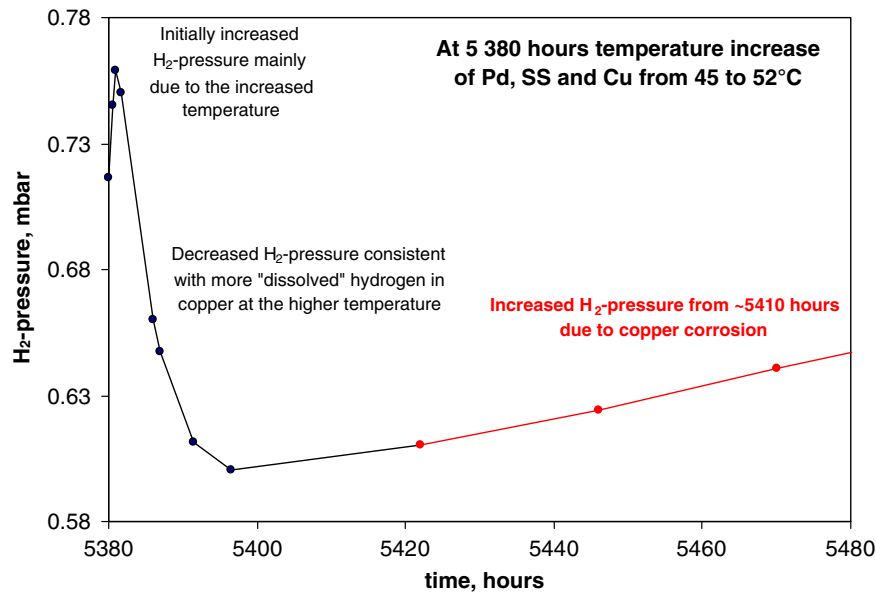


Fig. 4c. Detailed display of measurements of H₂-pressure above membrane with possible interpretations.

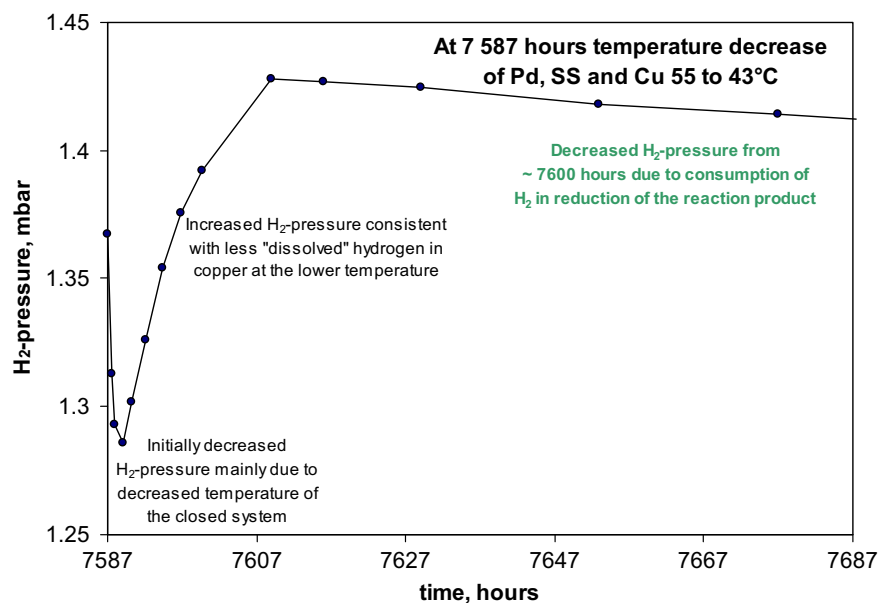


Fig. 4d. Detailed display of measurements of H₂-pressure above membrane with possible interpretations.

product with water molecules as the product. This catalytic property influences the observed equilibrium hydrogen pressure which greatly exceeds the hydrogen pressure in air. Dissociation of most molecular gases is expected to have a strong material dependency [10]. If the reduction of the reaction product is ruled by dissociation of H₂ our observed equilibrium is not a strict thermodynamic equilibrium but “only” a steady state. Moreover, we should always expect a dynamic situation at a molecular level both at a thermodynamic equilibrium and at a steady state.

Also the grain size may influence both the equilibrium hydrogen gas pressure and the kinetics below that equilibrium pressure due to different bonding in grain boundaries compared to grains.

4.2. Measurements with SIMS

It has been observed for many years that hydroxide can be related to a poor protective ability of an oxide [14]. In view of this

it is important and interesting that we should rather expect an initial CuOH formation than an initial hydrogen-free copper oxide formation [4]. We have exposed Cu to a high concentration of OH⁻ ions by the addition of NaOH to distilled water giving a pH ~13. In this exposure with air-contact a relatively fast reaction on Cu took place. This reaction could, as in distilled water, be seen as a consequence of reaction of metallic Cu with the OH⁻-ion.

The analytical technique of SIMS is capable of detecting hydroxide and its fragments. In Fig. 6 is SIMS-ratios from the exposure in the NaOH solution are shown. This figure clearly shows no detection of O/Cu in the outer part of the profile but only CuO/Cu. This can be caused by transformation of a copper hydroxide during the air contact. The O/Cu signal maximizes around 800 nm which then seems reasonable since the O/Cu signal is expected to diminish when sputtering into the metal region.

Fig. 7 shows hydrogen-containing ions from the reaction product on Cu in Pd- and Pt-enclosed containers [14] together with the

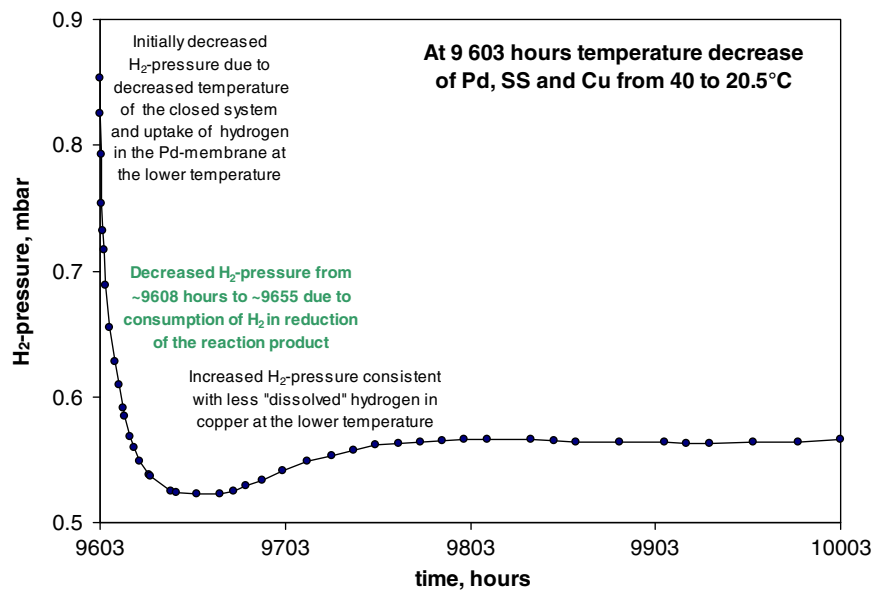


Fig. 4e. Detailed display of measurements of H_2 -pressure above membrane with possible interpretations.

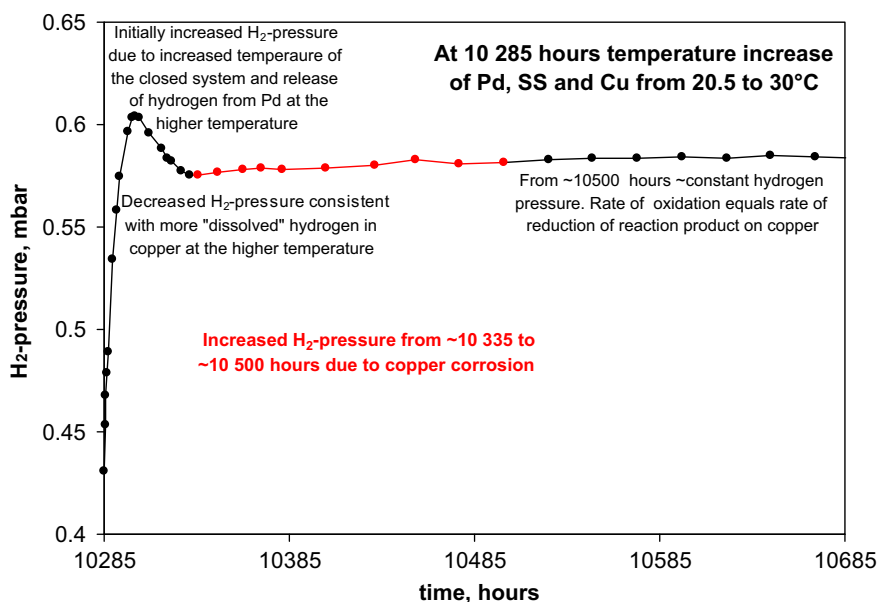


Fig. 4f. Detailed display of measurements of H_2 -pressure above membrane with possible interpretations.

short time exposure in the NaOH solution. In this figure, with the same analysis conditions, low counts in the exposure in the NaOH solution with air contact are observed. In this figure it is also seen that the container with a Pt-enclosure shows the highest count rates (ratio) and therefore indicates the highest H_2 -pressure in the 15 years exposure whereas the Pd-enclosed Cu shows the most uptake (ratio times thickness) of hydrogen among the profiles. Pd allows hydrogen transport much better than Pt and this difference between Pd-enclosure and Pt-enclosure has been further discussed in reference [15].

From the results on exposure in the pH ~ 13 NaOH solution we expect that oxidation of Cu takes place primarily by the ion OH^- . It is interesting to estimate the concentration of the ion OH^- in this exposure and in pure distilled water. We then find the concentration of OH^- is 10^5 – 10^6 higher in the exposure when NaOH was

added to distilled water compared to distilled water with no addition. This number is actually roughly the same as the reaction rate ratio in Fig. 7 corresponding to a few minutes compared to 15 years exposure of Cu.

4.3. General discussion

The OH^- -ion is often ignored since other ions, like chloride and sulphide are often present which overshadow the effect of this ion. The proton-content in water can always participate in an electrochemical corrosion process and therefore this can never be avoided in any liquid water. We point out the following issues we need to quantify to properly predict the H_2 -equilibrium (steady state) pressure in the gas volume and hydrogen into the Cu substrate from Cu corrosion in distilled water:

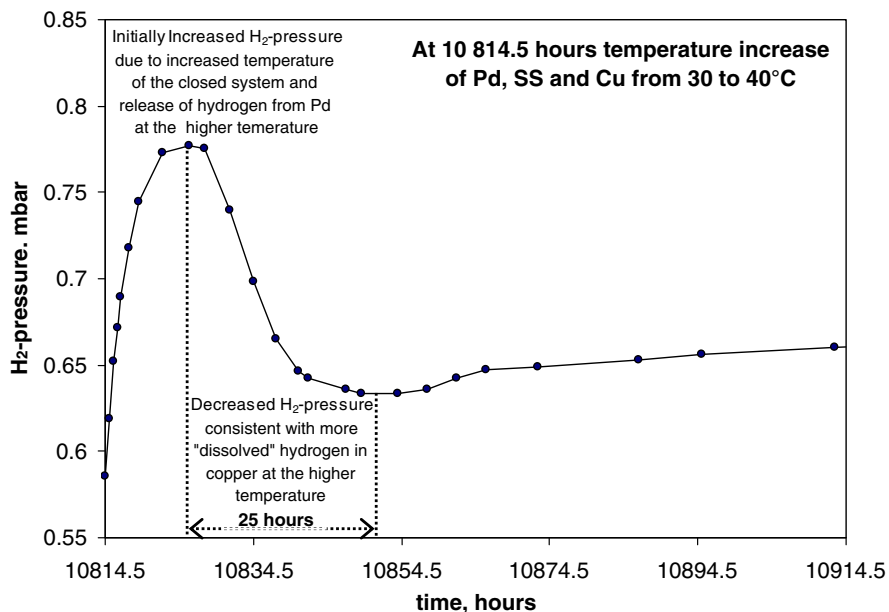


Fig. 4g. Detailed display of measurements of H₂-pressure above membrane with possible interpretations.

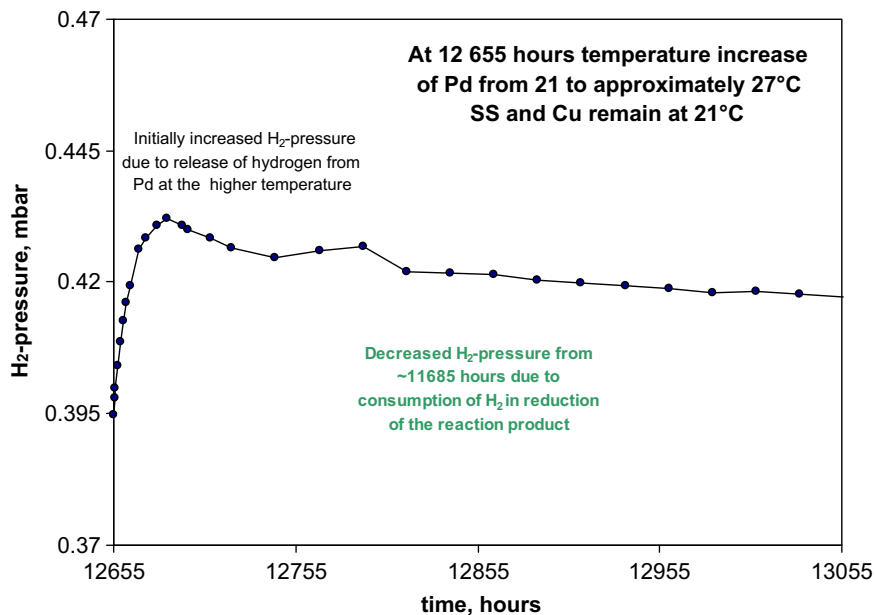


Fig. 4h. Detailed display of measurements of H₂-pressure above membrane with possible interpretations.

1. Dissociation rate ($H_2 \rightarrow 2H$) of molecular hydrogen on the actual reaction product.
2. Effects of grain-boundaries in the actual Cu sample.
3. Stability of CuOH in 2 and 3 dimensions including grain-boundaries.
4. Hydrogen related energies and transport in the Cu sample.
5. Since no material has a zero diffusion of hydrogen, the material in the enclosure of the Cu–water system can have an impact on Cu corrosion.

How efficiently can the hydrogen molecule reduce a reaction product on Cu? Obviously we need to know the rate of atomic hydrogen production from molecular hydrogen on the actual

reaction product to predict any required H₂-pressure. This is a key-point in corrosion of Cu by water where always OH⁻ and H⁺ ions are present and thereby also the possibility of $H^+ + e^- \rightarrow H$. We have measured the H₂-dissociation rate of 20 mbar hydrogen gas by means of hydrogen isotopes on an oxide on Zircaloy to be 10^{-9} of what is theoretically possible. It is possible (hypothetically) that all H₂-molecules impinging on the surface [9] will dissociate to 2H. In reality, H₂ can have a probability of only $\sim 10^{-9}$ to form H [10]. This means that the reduction ability of H₂ on the reaction product on Cu is far less than often calculated and we can find $\sim 10^{-3}$ bar as the H₂-pressure at equilibrium (steady state) even for formation of a hydrogen-free copper oxide. The measured points in Fig. 5 are, according to this

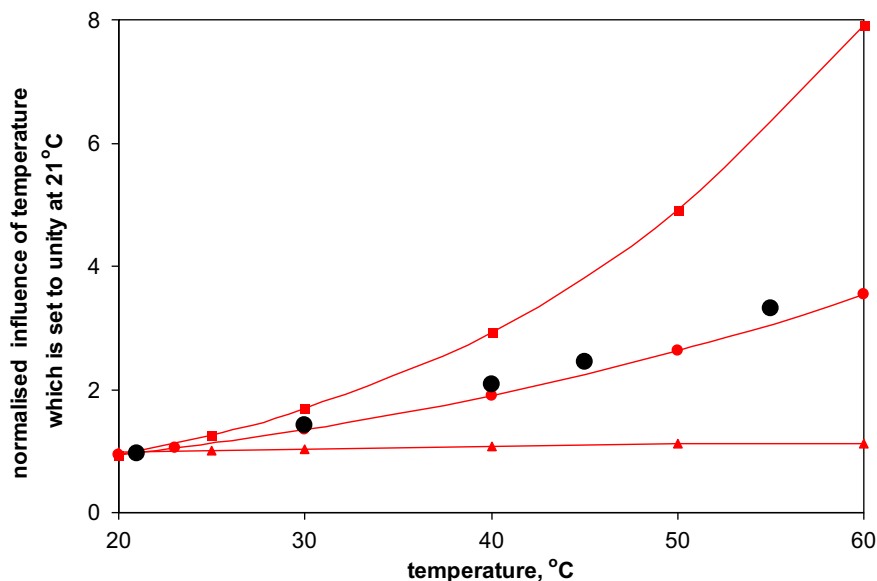


Fig. 5. Normalised measured H₂-pressure at equilibrium (steady state) of Cu corrosion at different temperatures in distilled water from Figs. 4a and 4b (●). Measured hydrogen pressure is 0.395 mbar at 21 °C, 0.584 mbar at 30 °C, 0.853 mbar at 40 °C, 1.009 mbar, 45 °C and 1.368 mbar at 55 °C. Normalised presence of OH⁻ from ion product [OH⁻][H⁺] (●). The ion product in distilled pure liquid water results in equal concentrations of OH⁻ and H⁺, [OH⁻][H⁺]. Normalised water vapour pressure in a closed system (▲). Data are normalised to unity at 21 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

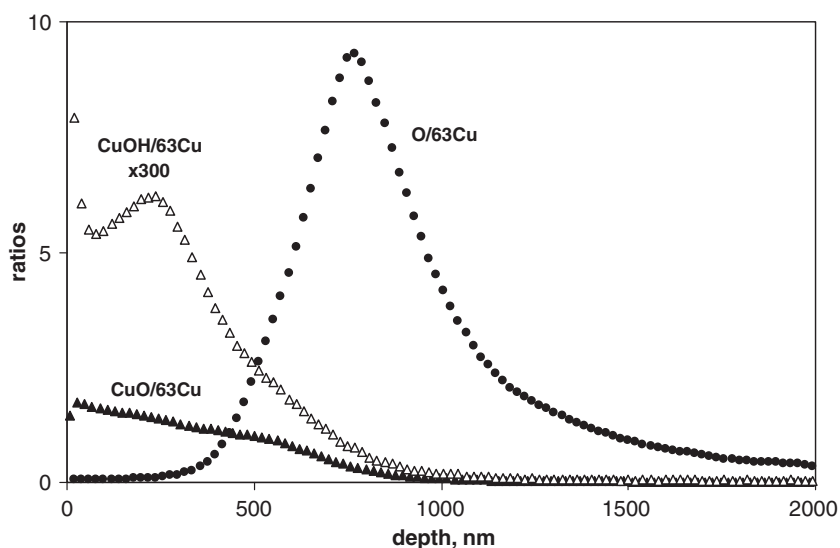


Fig. 6. Analysis of reaction products on polished Cu from SIMS after 5 min in NaOH added to distilled water with air contact. Addition of NaOH gave approximately pH13. Reaction product exposed a few minutes in 1 bar air before entry into the SIMS spectrometer. Ratios extracted from SIMS-analysis of O, ⁶³CuO, ⁶⁵CuOH, ⁶⁵Cu and ⁶³Cu ions.

discussion, from steady-states and not from strict thermodynamic equilibria.

One role of molecular oxygen is to form “new” water molecules ($2\text{H} + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$) and therefore molecular oxygen can be linked to the cathodic reaction $\text{H}^+ + \text{e}^- \rightarrow \text{H}$. For release of molecular hydrogen from a corroding surface there is most often a requirement of no molecular oxygen to the same surface. Accordingly, molecular oxygen can lower the effective activity of hydrogen in a decisive and beneficial way.

A clear drawback in electrochemical measurements of corrosion of Cu by water is the limited spatial resolution and the low conductivity of pure water. The potential measured between a standard electrode and the sample under study (OCP) can be the result of a mixed potential of the corroding sample and therefore hardly

helpful for the understanding of the present slow corrosion of Cu. The position of the hydrogen-electrode in Pourbaix-diagrams clearly says that no bubbles are expected when Cu is immersed in distilled water. Instead we need to consider the relatively low concentration of molecular hydrogen in our atmosphere if we want to make a prediction of the corrosion where Cu is in contact with water. An attempt, with a certain displacement of the existing hydrogen electrode in the potential-pH diagram, was made 25 years ago in this journal [1].

5. Conclusions

Corrosion of Cu has been studied via weight loss measurements and the following two conclusions are drawn:

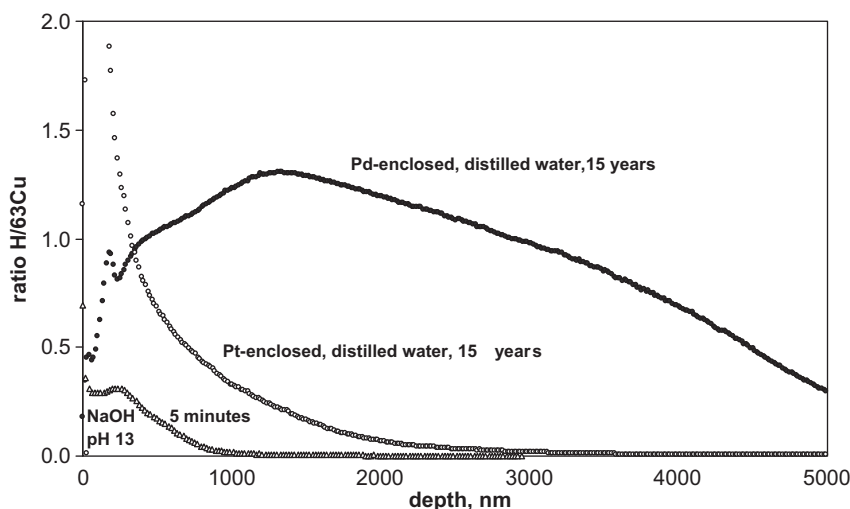


Fig. 7. Exposure for 15 years with enclosure of Pt and Pd. Exposure for 5 min in distilled water with addition of NaOH giving approximately pH 13. Ratios from SIMS analysis of H and ^{63}Cu ions.

1. Corrosion of Cu can be approximated by a weight loss at sufficiently high water access. At low water access a weight gain is observed.

2. There is a negligible influence when 1 bar of O_2 gas is bubbled in the water except at $\text{pH} \leq 4$.

Corrosion of Cu immersed in distilled water has been studied for 13,800 h in a closed system at 21–55 °C.

Based on the measured hydrogen gas pressure above the immersed Cu the following conclusions are made:

1. After removal of air in the closed system hydrogen gas is evolved to approximately 10^{-3} bar from corrosion of Cu which greatly exceeds the hydrogen gas pressure in the atmosphere which is tabulated as 5×10^{-7} bar.

2. There is a distinct temperature dependency of the time independent hydrogen gas pressure. This equilibrium corresponds to the situation where the rate of reduction of reaction product equals the rate of corrosion of metallic Cu.

3. The observed temperature dependency of the hydrogen gas pressure at equilibrium has, within error limits, the same temperature dependency as the concentration of OH^- in the ion product, $[\text{OH}^-][\text{H}^+]$. This ion product is a consequence of partial dissociation of water and increases with temperature but is always present.

4. The present mode of corrosion depends on the concentration of hydrogen in the Cu-samples and therefore their thickness.

5. The detailed measurements of H_2 are consistent with diffusion of hydrogen in Cu with a diffusion coefficient in the order of 10^{-13} to $10^{-12} \text{ m}^2 \text{ s}^{-1}$ near room temperature.

6. The presence of OH^- and H^+ facilitates a corrosion couple in corrosion of Cu in distilled liquid water.

7. The significance of OH^- and H^+ ions is similar to that in well-documented ultra high vacuum studies of Cu surfaces exposed to water at low pressures in which the concentration of these ions at the solid Cu surfaces was very low but still important.

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Appendix

For a continuous and sustainable detection of hydrogen gas, the production has to exceed the consumption rate in the detection. In

our detection of hydrogen gas, a mass spectrometer was continuously pumped with an ion-pump and the detection was taken at 5500 h (see Fig. 4a). Schematics of the display of the mass spectrometer are shown in Fig. 8.

The H_2 -production from Cu corrosion was monitored during 15 h with a mass spectrum up to 50 m/e every 2 min without any significant change of hydrogen gas signal in the mass spectrometer nor measured hydrogen gas pressure. The low base pressure of hydrogen gas in the mass spectrometer, $\sim 10^{-13}$ bar, was reached mainly due to hydrogen from the titanium in the pump elements being removed by heating under ultra high vacuum in another ion pump. (Commercial titanium normally contains ~ 20 wt ppm hydrogen.)

We can estimate the detected rate of H_2 -production from the nominal ion-pump rate, ion-pump current measured and the mass spectrum obtained:

Nominal ion-pump rate 100 l s^{-1} .
 Measured ion-pump current $1 \mu\text{A}$.
 Detected H_2 - pressure $3 \cdot 10^{-10}$ torr.
 Mole gas at 1 bar in $1 \text{ dm}^3 \sim 0.04$.
 This gives a detection $\sim 5 \times 10^{-8}$ mole H_2 in 24 h.

The production rate of H from the 140 cm^2 Cu sheets corresponds to a measured pressure rise of 0.02 mbar in the 0.12 dm^3 volume in 24 h. With the density of Cu of 8.9 g cm^{-3} and one

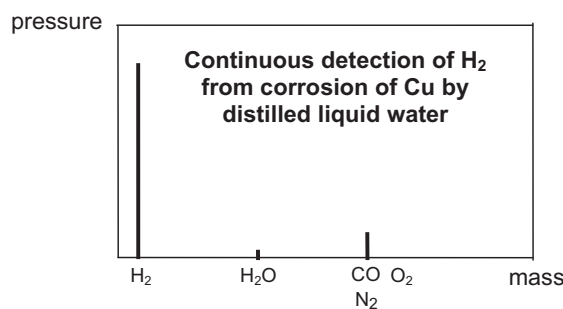


Fig. 8. Hydrogen gas (H_2) from corrosion of Cu displayed in a mass spectrometer. Mass spectrometer is placed in an ion-pumped ultra high vacuum chamber with base pressure $\sim 5 \times 10^{-10}$ mbar. Apart from hydrogen gas, the base pressure is mainly made up from pressure of H_2O , CO and N_2 . These are background gases in the mass spectrum and are not due to the corrosion of Cu.

produced H per produced CuOH this also gives 5×10^{-8} mole H₂ in 24 h. In this estimate it is also assumed that 50% of the released hydrogen (originally protons) is going into the metal and the other 50% goes to the gas phase where it is detected as H₂.

The value of 5×10^{-8} mole H₂ in 24 h corresponds to a corrosion rate of approximately 1 μm per year which is also reasonable for Cu corrosion at the measured temperature of 52 °C.

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