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**DETECTION OF HYDROGEN IN CORROSION OF COPPER IN PURE WATER**

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**ABSTRACT**

Copper is generally assumed to be immune to corrosion by water itself. However, this is not supported by any scientific experimental evidence. Corrosion results from 15 years of exposure are presented here. A transition from  $O_2$ -consuming to  $H_2$ -evolving copper corrosion is concluded, which implies that copper can corrode by water itself. The complex corrosion product contains hydrogen. We have also measured a hydrogen uptake in the copper metal as a result of metallic copper corrosion by water which implies a sample thickness dependence on hydrogen uptake. The results are described in terms of auto-ionisation of water which offers an explanation why copper corrosion can take place in pure  $O_2$ -free water.

Keywords: copper, corrosion, water, anoxic, auto-ionisation, hydrogen, SIMS

**INTRODUCTION**

Copper is assumed to be immune to corrosion by water itself<sup>1-3</sup>. One argument for this assumption is the existence of native copper in the earth's crust, but also metals such as Fe, Cr, Ti and Zn are found in the metallic state at some few locations<sup>4</sup>. In fact, this is also the situation for copper; only some per thousand of copper in the earth's crust exists in the metallic state and then concentrated to only a few locations<sup>5</sup>. This only proves that the hydrogen activity was high enough or that the water-, oxygen-, sulphur- chlorine activities were sufficiently low for geological time periods at those few geological locations. On the other hand, truly noble metals such as gold and platinum exist to at least 99% as native metals in the earth's crust.

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Results published twenty years ago from measurements of copper corrosion in water indicated that the assumption of copper immunity in water was wrong<sup>6,7</sup>. The equilibrium concentration of hydrogen in the atmosphere is virtually zero ( $10^{-42}$  bar) while the actual concentration in the atmosphere,  $5 \times 10^{-7}$  bar results from a steady state, determined by sources and sinks of hydrogen<sup>8</sup>. Copper corrosion in water is based on an assumption of a hydrogen free copper oxide ( $\text{Cu}_2\text{O}$ ) with an equilibrium hydrogen pressure  $p_{\text{H}_2} \approx 10^{-16}$  bar at  $20^\circ\text{C}^{1-3}$  and an interpretation of conventional potential-pH diagrams where the copper immunity range extends well above the hydrogen electrode potential ( $p_{\text{H}_2} = 1$  bar).

In previous isotope studies with gas mixtures of  $^{16}\text{O}_2$  and  $\text{H}_2^{18}\text{O}$  it was demonstrated that most of the oxygen in the corrosion product on iron<sup>9</sup>, chromium<sup>10</sup> and copper<sup>11</sup> originates from reaction with the water and not the oxygen. For these metals a considerable part of the consumption of the  $\text{O}_2$  takes place via the hydrogen-oxygen reaction ( $2\text{H}_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{H}_2\text{O}$ ) where adsorbed H is produced from the reaction of metal with water. The surface catalysed hydrogen-oxygen reaction is faster than the formation rate of the initially atomic hydrogen from the corrosion reaction itself on iron and copper<sup>11</sup>. This means that it is not possible to detect any hydrogen release from copper and iron as long as the supply rate of  $\text{O}_2$  to the surface exceeds the rate of hydrogen generation.

To our knowledge, the hydrogen pressure required to mitigate copper corrosion in water near room temperature has not been experimentally determined and therefore the assumption of copper immunity in water is lacking experimental evidence. On the contrary, in recent publication<sup>12</sup> we have demonstrated that the equilibrium hydrogen pressure exceeds the  $10^{-3}$  bar range instead of  $10^{-16}$  bar as interpreted from conventional potential-pH diagrams at room-temperature. This difference in equilibrium pressure, at least 13 decades, can only be explained by formation of a corrosion product that is more stable than  $\text{Cu}_2\text{O}$  in anoxic ( $\text{O}_2$ -free) water. As we have already indicated, this corrosion product exists and it contains hydrogen<sup>12</sup>. In fact, it is concluded by in-situ methods that the first product formed on a copper surface immersed in water is a copper hydroxide<sup>13,14</sup>.

## EXPERIMENTAL PROCEDURE

Copper samples were exposed in deionised water at room temperature for 15 years in two different set-ups. The metal was in the form of 0.1 mm foils (temper: annealed) and 2 mm rods (temper: as drawn) respectively. In all experiments copper was mechanically polished with 600-1000 mesh SiC-paper immediately before immersion in water. The exposures are summarised in Table 1.

**TABLE 1.**  
**EXPERIMENTAL CONDITIONS FOR EACH GLASS-CONTAINER WITH DISTILLED WATER AND COPPER SAMPLES EXPOSED FOR 15 YEARS**

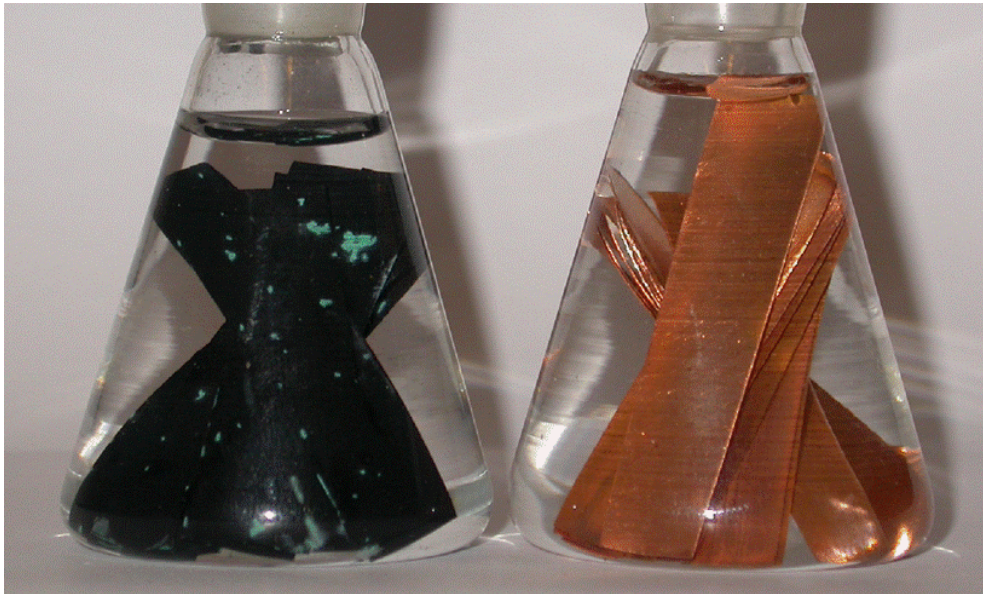
Container	Conditions	Copper samples	Figs.
E-flask	Hydrogen permeable enclosure	Foils OFHC 99.95+%	1-4
E-flask	Gas tight enclosure (only glass)	Foils OFHC 99.95+%	
Test tube	Hydrogen permeable enclosure	Rod OFHC 99.99+%	5-6
Test tube	Gas tight enclosure (Pt, glass)	Rod OFHC 99.99+%	

The containers used were made of glass such as borosilicate and not quartz glass which should not be used due to a high transport of hydrogen at room-temperature. The water volumes in the E-flasks were identical in the beginning,  $50 \text{ cm}^3$ , with approximately  $1 \text{ cm}^3$  of air. The exposed surface area of copper was  $85 \text{ cm}^2$  in each flask. A 0.1 mm Pd- foil with sufficient area was used as a hydrogen membrane. The

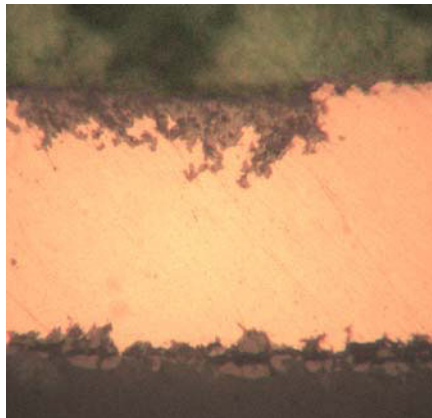
glass-containers were hermetically sealed with UHV-glye (Varian Vacuum Technologies). The post examination of the surface and cross-sections were performed with light optical microscopy, Field emission gun scanning electron microscopy (FEG-SEM). The corrosion products on the exposed foils were also analysed with Electron spectroscopy for chemical analysis (ESCA). Secondary ion mass spectroscopy (SIMS) was used to analyse the formed adhering solid product on the exposed rods. In this analysis the copper rods were exposed to air for as short a time as possible.

## RESULTS AND DISCUSSION

Fig. 1 shows the appearance of copper foils after 15 years exposure in distilled water. Fig. 2 shows a cross-section of a green area seen in Fig. 1.

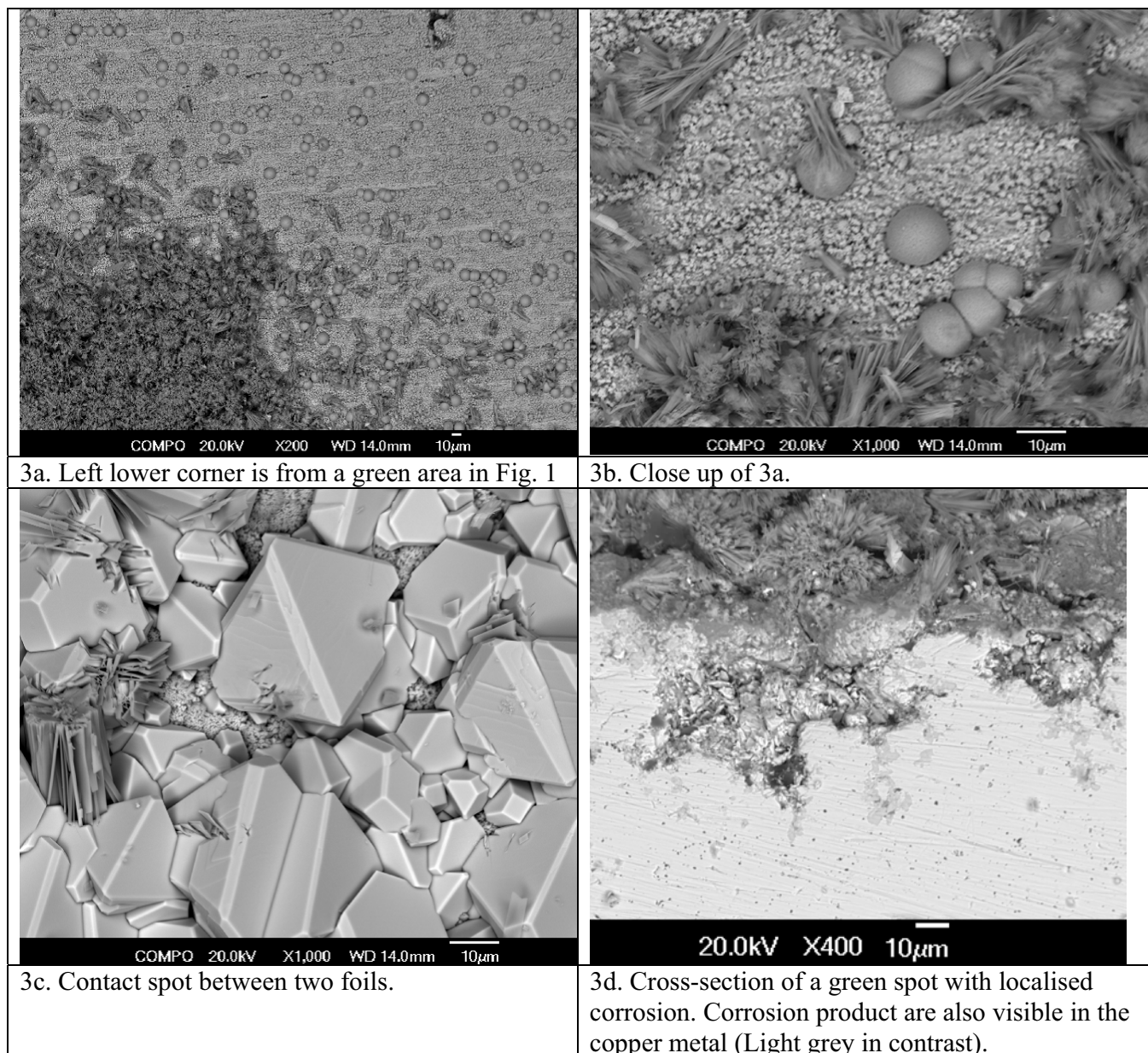


**FIGURE 1 – Appearance of copper after 15 years of exposure in distilled water at room-temperature. Hydrogen from corrosion can escape from the left container but not from the container to the right. The water volume was equal in the flasks in beginning of the exposure.**



**FIGURE 2 – Light optical cross-section of the initially 100µm metallic copper foil after 15 years exposure in distilled water. Localised corrosion attack is clearly visible.**

In Fig. 3, a FEG-SEM characterisation with EDX has been used. The SEM-micrographs 3a and 3b are from regions with free access to water and 3c with limited access to water due to a contact spot with another foil. As seen, there are a variety of different structures of corrosion product despite the simple system of pure water and copper.

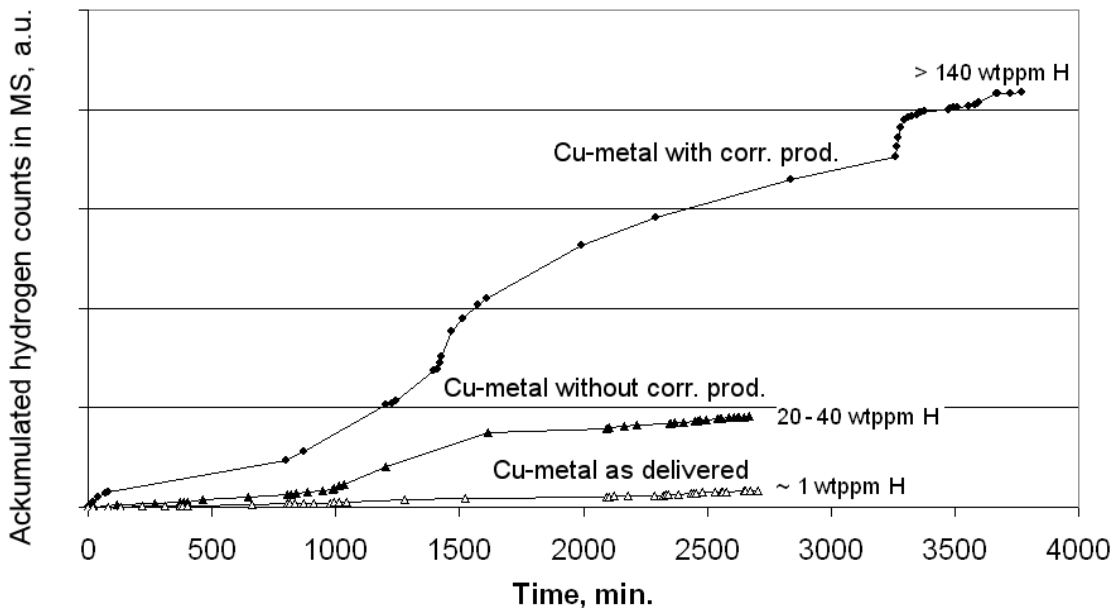


**FIGURE 3 – FEG-SEM secondary electron images of reaction products from the left container in Fig. 1, where 3d is a cross-section. 3a and 3b are from regions with free access to water and 3c with limited access to water due to contact with another foil. The chemical composition, based on EDX analysis (hydrogen excluded), of the products in direct contact with water were in the range of 44-52 atomic-% oxygen and the rest was copper. This analysis also includes the green spots. The composition of the crystal structure in 3c was 28 atomic-% oxygen and 72 atomic-% copper.**

A clear localised corrosion is visible in the cross-sections shown in Figs. 2 and 3d which has never been reported before in pure water. Copper oxides are found in connection to green areas down to a depth of

around 70  $\mu\text{m}$  from the original surface. Hence a local copper corrosion rate of approximately 5  $\mu\text{m}/\text{y}$  can occur in anoxic water. This rate is similar or higher to the corrosion rate found in oxygen-containing waters<sup>15</sup>. It is not surprising that corrosion in grain boundaries is observed when more ions than  $\text{OH}^-$  and  $\text{H}^+$  are present from auto-ionisation. Such a corrosion phenomenon has recently been reported<sup>16</sup> in the presence of  $\text{HS}^-$  and  $\text{Cl}^-$ .

In Figure 4 it is shown by thermal out-gassing that the corrosion product and also the underlying metal contains hydrogen as a result of this exposure. The method of quantitative out-gassing of hydrogen has been described earlier<sup>17</sup> and in Table 2 some results are collected from various copper samples.



**FIGURE 4 – Integrated removal rate of hydrogen in a mass spectrometer (MS) by outgassing at 20-700°C of corrosion product and underlying “metal”. Unexposed copper is taken as a reference. The calculated hydrogen concentrations are also indicated.**

**TABLE 2  
HYDROGEN CONCENTRATION IN COPPER MEASURED BY THERMAL OUT-GASSING.**

Copper sample	wtpm hydrogen
Cu-gasket 2 mm, stored 25 years in air	~0.2
Cu-OFP copper (Intended for final storage in Sweden)	0.3
Foil, 0.1 mm. OFHC 99.95+ as delivered	1.5
Foil, 0.1 mm. OFHC 99.95+ exposed 15 years in anoxic water	6-40 <sup>1</sup>

1) Measured after removal of surface corrosion products. The higher values could partially be due to remaining internal corrosion products which are seen in Figure 3d (light grey in contrast).

The hydrogen concentration in copper in thermodynamic equilibrium with 1 bar  $\text{H}_2$ -gas at RT is  $\ll 0.1$  wtpm. As shown in Table 2, copper metal is normally hydrogen “charged” to some extent also in the as delivered condition and up to ten times higher after the 15 years exposure which indicates a high hydrogen activity due to corrosion in anoxic water. This means that the anoxic corrosion process can result in slow hydrogen charging and consequently there must be a sample thickness and time dependence on the hydrogen concentration in the metal. This also implies that the corrosion product is influenced by sample thickness and time. Therefore, a degradation of the protectiveness of a copper

oxide film in anoxic environments due to hydrogen and/or hydroxides seems plausible which can result in a more porous corrosion product as seen in Figs. 2 and 3. In fact it is observed that hydrogen in various metals is detrimental to the protectiveness of the passive film<sup>18-20</sup>. It is indicated that the general belief of formation of a dense protective “passive film” on copper in pure water is wrong, at least after 15 years of exposure. It could be added that the mechanical properties of the exposed copper may be reduced due to the hydrogen uptake based on the fact that the foil required only one 180° bending to initiate a crack. In fact, it is known that the mechanical properties of copper are reduced due to hydrogen uptake<sup>21</sup>.

Palladium can be used to collect hydrogen from an atmosphere and subsequently be removed by out-gassing in vacuum. Earlier we have studied the hydrogen-oxygen reaction on palladium in water and in ambient air and found that this reaction is fast in ambient air due to the presence of a high concentration of oxygen in this environment<sup>22</sup>. Another application of palladium in corrosion research is to use it as a hydrogen permeable membrane as shown in the lower part of Fig. 5.



**FIGURE 5 –. Appearance of copper after 15 years of exposure in distilled water at room-temperature. Hydrogen is allowed to escape via the palladium membrane from the lower tube but virtually not from the upper tube which has a platinum membrane. The membranes are sealed with UHV-glue (white).**

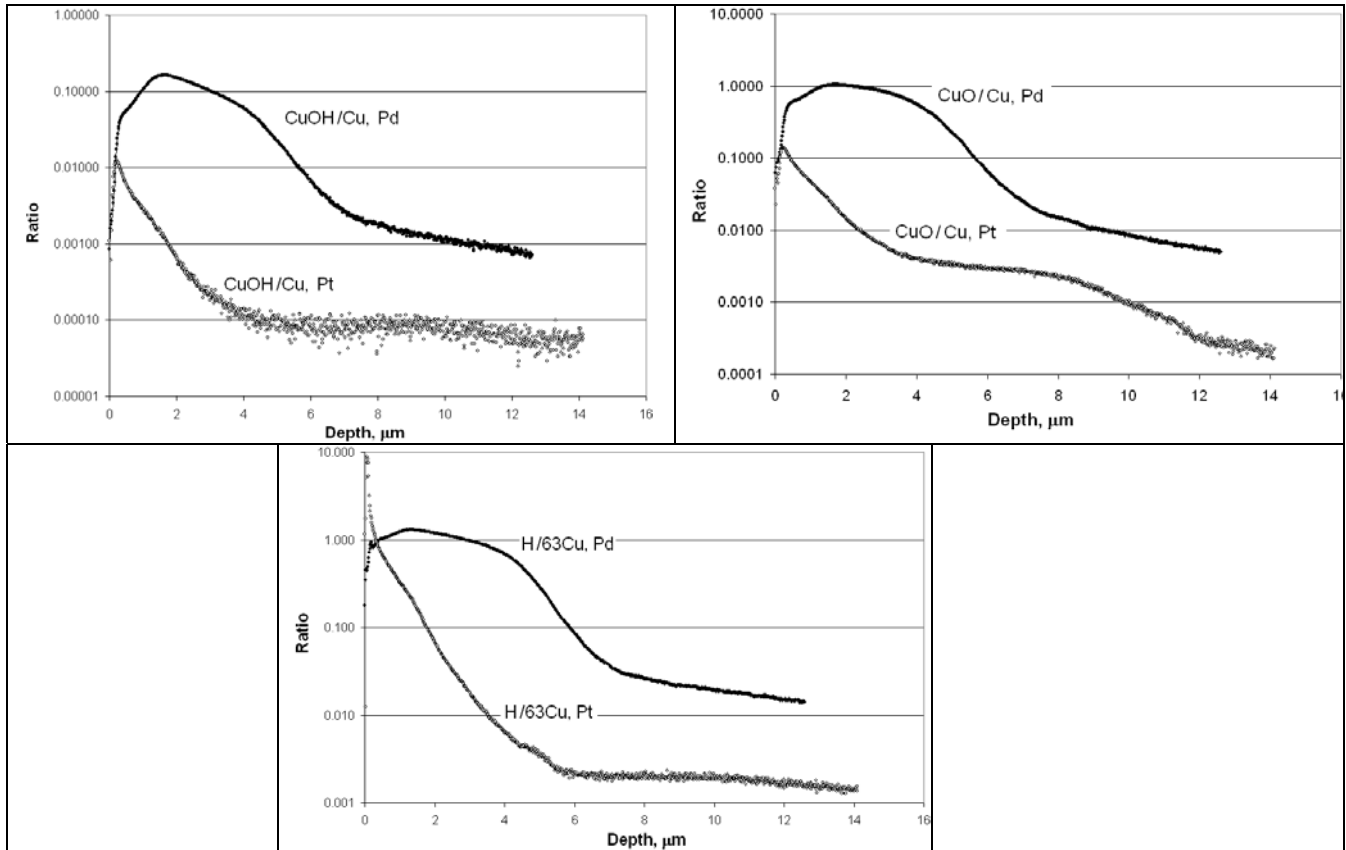
SIMS-analysis has been applied on the surfaces of copper rods seen in Fig. 5. In spite of the fact that ionisation in SIMS is complex<sup>23</sup> it is shown here with this technique that the corrosion product contains considerable amounts of hydrogen. The samples were exposed to ambient air for less than 10 minutes before they were placed in vacuum for SIMS analysis. This time was as short as possible to minimize the conversion of hydroxides to oxides due to air exposure<sup>13</sup>. Ratios from this analysis are shown in Fig. 6 which clearly shows a role of OH in the corrosion and hence a hydrogen containing product is formed and not the simple  $\text{Cu}_2\text{O}$  as a result of anoxic oxidation by water. Furthermore, SIMS-analysis has also been applied on a cross-section of the copper rod in the tube with palladium. This analysis showed a significant influence of the exposure down to least 0.2 mm from the outer surface.

An even more striking result is the difference in corrosion between palladium and platinum membranes as part of the enclosure in Fig. 5. The reason for this difference is that hydrogen can leave the corroding system via palladium but virtually not via platinum. This means that corrosion can continue unimpededly in the case of palladium since the equilibrium pressure of hydrogen is never reached in this case. The presence of hydroxides in the corrosion product is also supported by ESCA analysis of the foils exposed for 15 years.

It is also interesting to consider the well established view<sup>24</sup> of an outer hydroxide in atmospheric corrosion and its consequences. That view should include the “left over” of hydrogen when the

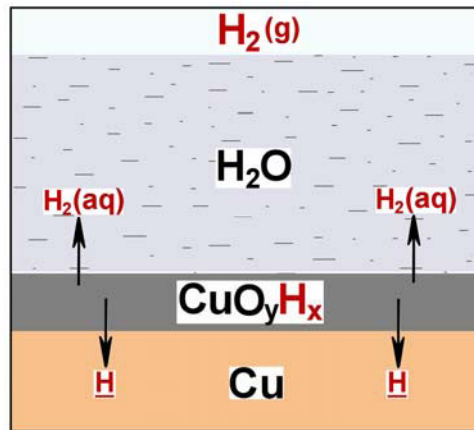
hydroxide comes from water and the possibility that  $O_2$  is consumed via formation of “new” water in the hydrogen-oxygen reaction. This scenario can explain earlier experimental results in <sup>9-11</sup> where isotopes were used to show that water is formed and oxygen in the “new” water comes from  $O_2$ .

The effect of the anion  $OH^-$  is often overshadowed by effects of stronger anions like  $Cl^-$  and  $HS^-$  but in pure water the ion  $OH^-$  can manifest itself. The role of auto-ionisation of water and its temperature dependency is not defined in a gas but only in a liquid. Then, also the adsorbed water may be a precursor to auto-ionisation.



**FIGURE 6 – Hydrogen and oxygen-containing ions in SIMS-profiles normalised to copper ions. The influence of Pd and Pt as membranes is clearly seen.**

In summary, atomic hydrogen is produced when copper corrodes in pure water, i.e. copper reacts with the  $OH^-$ -ions from auto-ionisation and the protons form hydrogen. Fig. 7 shows schematically that the produced hydrogen from copper corrosion can be found in the metal, product, water and in the gas phase.



**FIGURE 7 – Principal pathways for released hydrogen from copper corrosion in a closed system with pure water.**

### CONCLUSIONS

- Critical experiments show that copper is corroded by water itself, i.e. via auto-ionisation of water.
- Hydrogen is detected by SIMS in the adhering corrosion product which is consistent with ESCA results. It is clear that a hydrogen-containing copper corrosion product exists which is more stable than  $\text{Cu}_2\text{O}$  in anoxic environments.
- An increased hydrogen concentration was also measured in the copper metal which implies a hydrogen uptake due to anoxic corrosion.
- The localised anoxic corrosion rate of copper can be higher than the general corrosion rate in  $\text{O}_2$ -containing water.
- The protectiveness of the “passive film” on copper is suggested to be reduced when exposed to pure anoxic water in the long term. This can be due to the presence of hydroxides and hydrogen in the “passive film” and in the metal respectively.
- Long term experiments have also indicated that the mechanical properties of the exposed copper are reduced which could be related to the observed hydrogen uptake in the copper metal.

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