



Corrosion of Copper by Water

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We have studied copper corrosion in a system comprised of deionized water, absolute pressure gauges, and a palladium membrane. A transition from O₂-consuming to H₂-evolving copper corrosion is observed, which indicates that copper can corrode by water itself. The equilibrium hydrogen pressure in corrosion of copper by water at 73°C exceeds the steady-state atmospheric hydrogen pressure (5×10^{-7} bar) by a factor of about 2000. The growth of a hydrogen-containing corrosion product in O₂-free water is controlled by the hydrogen removal from the corroding surface. The results are discussed in the perspective of conventional potential-pH diagram for copper.

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Manuscript submitted January 22, 2007; revised manuscript received July 20, 2007. Available electronically August 23, 2007.

Copper is assumed to be immune to corrosion by water itself.¹⁻³ Results published 20 years ago from measurements of copper corrosion in water by using a commercial solid electrolyte hydrogen probe implied that this assumption was wrong.⁴ However, the sensitivity of the probe was disturbed by humidity and the measured hydrogen pressures could be questioned.⁵ The equilibrium concentration of hydrogen in the atmosphere is virtually zero (10^{-42} bar), while the actual concentration in the atmosphere (5×10^{-7} bar) results from a steady state, determined by sources and sinks of hydrogen.⁶ Copper immunity in water is based on an assumption of a hydrogen-free copper oxide (Cu₂O) with an equilibrium of $\text{pH}_2 \approx 10^{-16}$ bar at 20°C,¹⁻³ and an interpretation of conventional potential-pH diagrams where the copper immunity range extends well above the hydrogen electrode potential ($\text{pH}_2 = 1$ bar).

In previous isotope studies with gas mixtures of ¹⁶O₂ and H₂¹⁸O it was demonstrated that most of the oxygen in the corrosion product on iron,⁷ chromium,⁸ and copper⁹ originates from reaction with the water and not the oxygen. For these metals most of the consumption of the O₂ 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 are produced from the reaction of metal with water. The surface-catalyzed hydrogen-oxygen reaction is faster than the formation rate of the initially atomic hydrogen from the corrosion reaction itself on iron and copper.⁹ This means that it is not possible to detect any hydrogen release from copper and iron as long as the supply rate of O₂ to the surface exceeds the rate of hydrogen generation. Although these observations were made in gaseous water, the same principles may also apply to systems with dissolved O₂ in liquid water.

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.¹⁰ In the following, we present experimental data on the equilibrium hydrogen pressure for a corrosion process of copper in water at approximately 73°C. We further demonstrate that the corrosion product is a complex hydrogen-containing product. The concept of equilibrated ambient air,⁶ its consequences on copper corrosion in water, and the conventional potential-pH diagram for copper¹¹ are also discussed.

Experimental

Two, ultrahigh vacuum (UHV)-compatible, experimental arrangements were used in this study. In both arrangements 0.1 mm thick oxygen-free high conductivity copper (OFHC) 99.95+% copper foil (temper: hard) was used. The foil was polished with 1000 mesh SiC paper immediately before immersion in deionized water.

The palladium membranes were approximately 0.1 mm and were held at the same temperature or slightly higher than the water with the immersed Cu.

One arrangement, aimed for an ion pump experiment, was used for a study of Cu corrosion at room temperature with the use of an ion pump with a pump rate of 200 L s⁻¹ and a base pressure of approximately 1×10^{-12} bar. In this experiment a glass container with approximately 0.1 dm³ distilled water with a small gas volume was hermetically sealed with a palladium membrane and an UHV glue (Varian Vacuum Technologies). The measurable increase in pump current was preceded by a constant pump current corresponding to a pressure of approximately 1×10^{-12} bar.

The second arrangement, aimed for a pressure gauge experiment, is shown in Fig. 1 and consisted of two compartments, each with a pressure meter, separated by a palladium membrane.¹² Thereby the compartments could only communicate with hydrogen gas but no other gases.¹² The compartment which could detect only hydrogen gas was initially evacuated. Both compartments were made of stainless steel (AISI 316L) and exclusively based on UHV metal gaskets, as shown in Fig. 1. This arrangement was designed for direct pressure measurements of any hydrogen gas evolution resulting from copper corrosion by water. The volume of gas phase in the stainless steel vessel was 0.05 ± 0.005 dm³, the water volume 0.09 ± 0.005 dm³, and the isolated volume above the palladium membrane was 0.04 ± 0.005 dm³. An inner glass container (Duran) was used for the liquid water (with immersed copper) and therefore the stainless steel parts were only exposed to the gas phase. In this experimental setup it takes approximately 150 h at room temperature to reach an equilibration, ruled by diffusion, between the gas phase and dissolved gases in the liquid water. After equilibration, a measured pressure decrease is interpreted as oxygen consumption and consequently, a constant pressure is interpreted as no measurable oxygen consumption. In addition, weight change measurements of the exposed copper foils were performed.

A blank experiment (without any immersed copper) was also performed in this second arrangement.

Results and Discussion

Ion pump experiment.— An experiment was performed at room temperature with the purpose of estimating the corrosion rate of copper in pure water by determining the hydrogen gas produced in the absence of any dissolved oxygen. Hydrogen diffused through the palladium membrane and was continuously pumped away with the ion pump, as shown by the schematically inserted experimental setup in Fig. 2. The experiment, which included cell and membrane, recorded in this figure was made at 20°C except for 100 h at 8°C. The hydrogen production rate is also measurable at 8°C, though with a lower rate of the H₂ evolution. An estimate of the H-flux, based on the well-established diffusion coefficient and membrane permeability of hydrogen in palladium,¹² gives a $\text{pH}_2 > 1 \times 10^{-9}$ bar in the gas phase above the water. This is at least six

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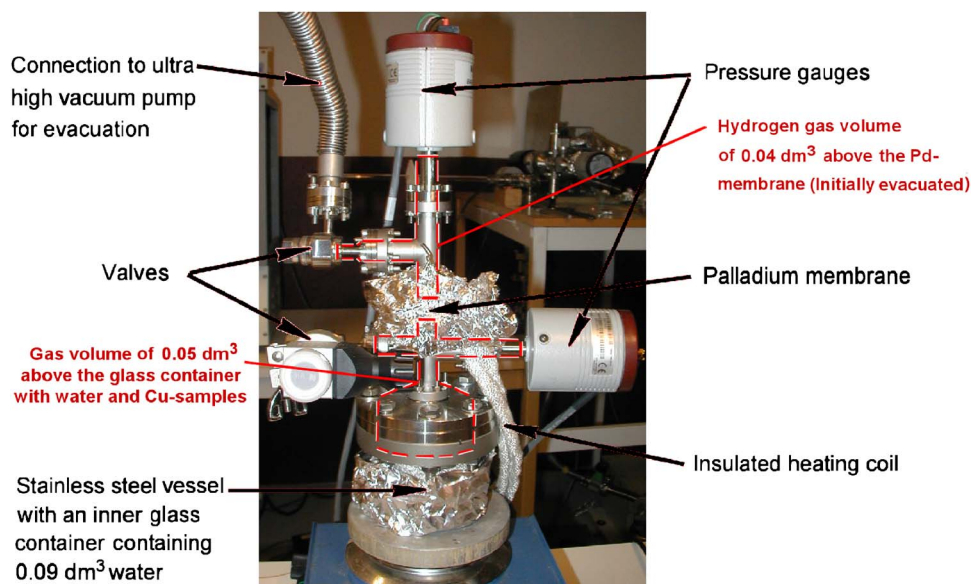


Figure 1. (Color online) Experimental UHV-compatible arrangement with pressure gauges for study of hydrogen release in metal corrosion. Two gas volumes, separated by a palladium membrane, are indicated.

decades higher than the theoretical hydrogen equilibrium pressure for the system Cu/Cu₂O/H₂O found in the literature.¹⁻³ At the end of the experiment the ion pump current corresponded to a hydrogen release rate of 0.37 ng h⁻¹ cm⁻² at the copper surface, which corresponds to a copper corrosion rate with the O₂-free water in the submicrometer range per year. A constant release rate of hydrogen was not obtained during the experiment despite the long time used, 11,000 h. This emphasizes the slow and not easily monitored corrosion of copper in anoxic (without dissolved oxygen) water at room temperature. From this experiment it is not possible to determine the equilibrium hydrogen pressure in the copper-water reaction, because the produced hydrogen gas was continuously removed from the gas phase above the immersed copper. Although not clearly indicated in Fig. 2, there was a 150 h delay for the onset of hydrogen gas release, which we interpret as the time required to consume residual oxygen in the system remaining from the small amount of air enclosed during the experimental setup.

Pressure gauge experiment.— In contrast to the ion pump setup, the apparatus in Fig. 1 enables direct measurements of hydrogen pressures as shown in Fig. 3. An initial partial evacuation of air and an equilibration between gas and water preceded monitoring of the decreasing total pressure, starting at 150 h in Fig. 3. As mentioned in the Experimental section, a total pressure decrease is interpreted as an O₂ consumption. In this way a total pressure decrease of 12.8 mbar gives the initial amount of O₂ in the 0.05 dm³ volume, which corresponds to 0.8 mg ± 0.1 mg O₂. After 1200 h the temperature was raised from 20 to 62°C, at 2100 h to 73°C, and at 2275 h to 85°C. Between 2293 and 2295 h several evacuations of the upper (only hydrogen-containing) volume were made. Virtually all dissolved oxygen was consumed after 1280 h, and at 1350 h the first significant hydrogen gas release (0.01 mbar) was observed above the water surface. A transition from oxygen-consuming to hydrogen-evolving copper corrosion was hence seen. The plateau in

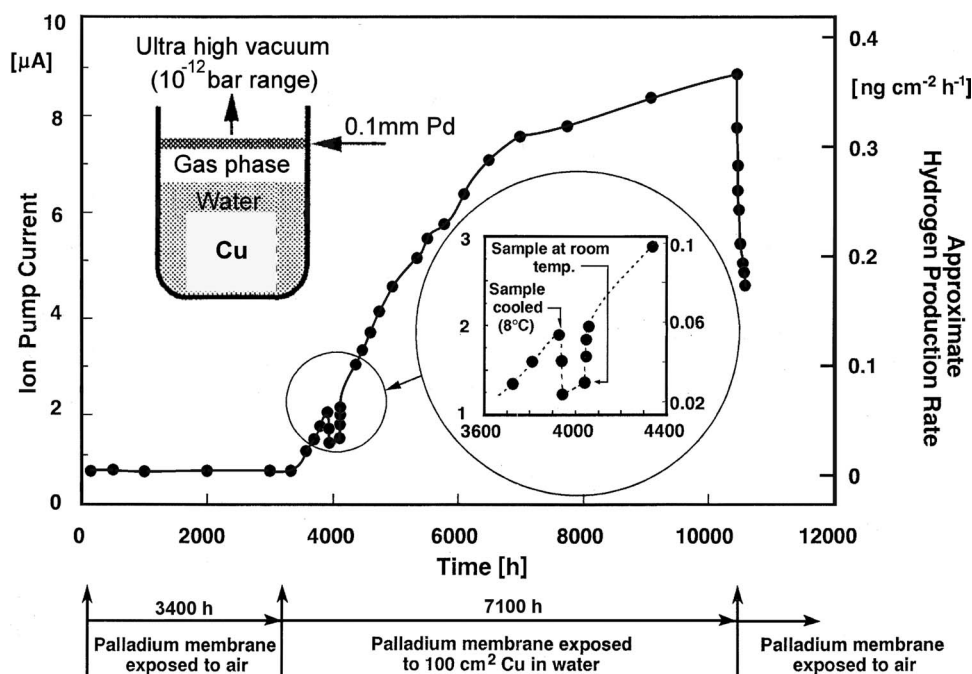


Figure 2. Ion pump experiment. The measured ion pump current is proportional to the rate of hydrogen permeation through the palladium membrane which corresponds to a hydrogen production rate. The temperature was near 20°C, except for 100 h at 8°C. Hydrogen is released during approximately 7000 h due to corrosion of copper in deionized water. The hydrogen production rate is 0.37 ng h⁻¹ cm⁻² copper after approximately 7000 h exposure. The container with copper and water was removed at 10,500 h and the palladium membrane was exposed to air.

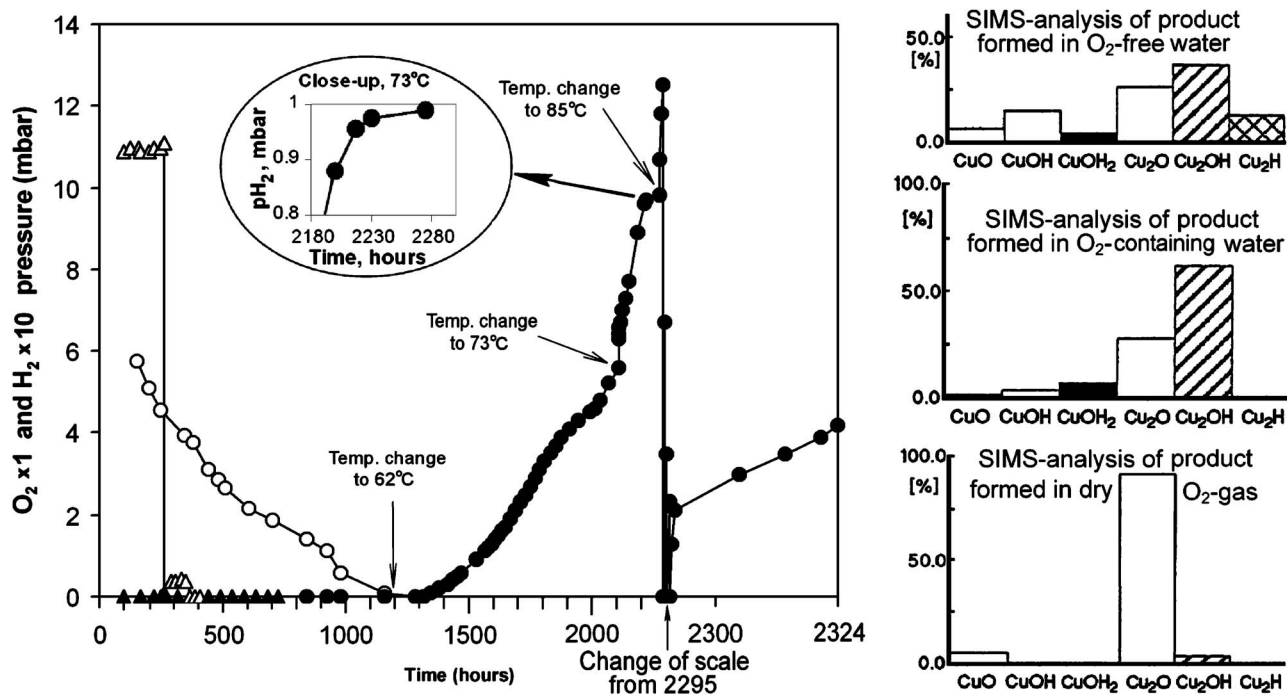


Figure 3. Pressure gauge experiment. Partial pressures of O₂ (open circles) and H₂ (filled circles) during exposure of copper to deionized water in equilibrium with 30 mbar N₂ (by the use of the experimental setup shown in Fig. 1). At time zero, the deionized water was enclosed with an air volume, which was evacuated for 3 s (dissolved gases still remained in the aqueous water). From the start to 1200 h the temperature was 20°C, from 1200 to 2100 h it was 62°C, from 2100 to 2275 h 73°C, and from 2275 to 2324 h 85°C. Between 2293 and 2295 h several evacuations of the upper (only hydrogen-containing) volume were made. An additional blank experiment (without immersed copper) is also included, where the partial pressures of O₂ (open triangles) and H₂ (filled triangles) are shown. Evacuations at 20°C of the gas phase were done initially, at 262 and 361 h respectively. After 406 h the temperature was raised to 63°C, and to 73°C at 509 h. This blank experiment was terminated at 726 h. The figure also shows the distribution of emitted ions in SIMS 3D sputtering of the reaction product formed in O₂-free water, in O₂-containing water, and in dry O₂ gas, respectively.

the hydrogen pressure vs time curve in the inserted closeup in Fig. 3 is interpreted as an equilibrium hydrogen pressure resulting from corrosion of copper in pure water at 73°C. This pressure, of about 1 mbar, exceeds the steady-state atmospheric hydrogen pressure (5×10^{-7} bar)⁶ by a factor of approximately 2000. By an independent analysis it is confirmed that the gas above the palladium membrane is hydrogen. The weight gain of the copper samples in this exposure was 1.5 ± 0.1 mg. An initial weight loss is expected due to release of Cu ions to the water followed by a weight gain resulting from formation of solid reaction products. This fact strengthens the observation that oxygen in the solid reaction product originates from water itself. As indicated above, virtually all O₂ (0.8 mg) was consumed by copper corrosion. We can conclude that approximately half of the weight gain, $(1.5-0.8)/1.5$, was due to a reaction with water.

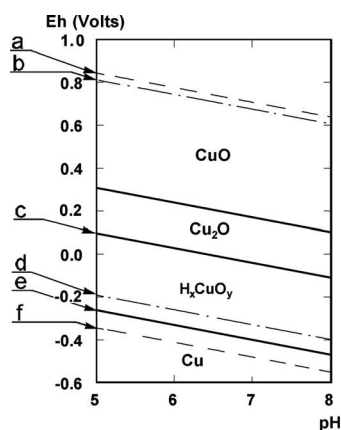
To further emphasize that copper can corrode by water itself, a blank experiment without any immersed copper was performed which also is shown in Fig. 3. Here three evacuations of the gas phase were done; initially, at 262 and at 361 h, respectively. The O₂ pressure was reduced from 210 mbar to 11 mbar during the first evacuation, as seen in Fig. 3. The following evacuations resulted in an O₂-pressure < 0.01 mbar during the subsequent 406–726 h blank exposure at 63°C and 73°C. At any time no H₂ was detected. This means that the immersed copper evolves H₂ after all O₂ is consumed. We have repeated exposure of copper in pure water and again measured a hydrogen pressure in the mbar range.

Solid corrosion product on copper and aspects of dissolved O₂ and H₂.— A considerable difference in chemical composition of the 3D-corrosion products formed in O₂-free water, in O₂-containing water and in dry O₂ gas, respectively, was recorded by secondary ion mass spectrometry (SIMS). This is also shown in Fig. 3. The product formed in O₂-free water contains more hydrogen compared

with the product formed in O₂-containing water. Furthermore, an additional hydrogen-containing species is detected in this analysis. The ratio of H/O in SIMS species under anoxic condition is close to unity, which also indicates a solid product with the same ratio of H/O.

Powder diffraction analyses [X-ray diffraction (XRD)] with Si as internal reference were performed on several different copper samples from the anoxic experiments. The spectra were consistent with CuO and Cu₂O, albeit somewhat distorted, especially regarding the tenorite (CuO), PDF-00-048-1548 and PDF 00-005-0661. As no known copper hydroxides were detected by XRD despite the high hydrogen content and the fact that all spectral lines could be linked to oxides, this indicates that H is in an “unusual” position in the solid product. It seems most likely that hydrogen is associated with copper ions and/or copper vacancies in the copper oxide crystals rather than forming crystalline hydroxides. Actually, in the research area of surface catalysis, copper-modified zeolites have been shown to adsorb/absorb hydrogen “unusually strong” due to the interaction between copper ions.¹³ Furthermore, hydrogen-copper clustering in Zn_{1-x}Cu_xO has been detected by neutron-scattering methods.¹⁴ As we have not made and, as far as we know, nobody else has made any in situ characterization of the corrosion product, we propose here that the corrosion product may be written as H_xCuO_y, where the average values of both *x* and *y* seem to be close to unity, at least after extended exposure times. The outer product could be described as a “protonated” cupric oxide, and it is likely that the product closest to the Cu metal is more like H_xCuO_{0.5}, which could be described as a “protonated” cuprous oxide.

It is shown in several metal oxide-hydrogen systems that hydrogen is detrimental to the protectiveness of the oxide film.^{15,16} This



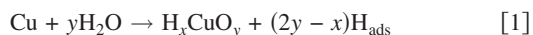
Line	Condition	O ₂ -gas (bar)	H ₂ -gas (bar)	Potential (at pH7)
a	Standard oxygen electrode.....	1	~10 ⁻⁴²	0.708
b	Water in equilibrium with equilibrated air.....	0.21	~10 ⁻⁴²	0.698
c	Cu ₂ O/H _x CuO _y -equilibrium.....	~10 ⁻⁵⁸	~10 ⁻¹³	0.039
d	O ₂ -free water in equilibrium with the atmospheric H ₂ -pressure..	~10 ⁻⁷¹	5×10 ⁻⁷	-0.304
e	* Measured and interpreted as H _x CuO _y /Cu-equilibrium.....	~10 ⁻⁸¹	~0.001*	-0.400
f	Standard hydrogen electrode....	~10 ⁻⁸⁴	1	-0.488

Figure 4. Calculated copper potential-pH diagram at 73°C¹¹ with an observed hydrogen-containing corrosion product (H_xCuO_y) formed under anoxic conditions at 73°C in deionized water. The equilibrium of formation of this product from Cu is represented by line (e), and the close position just above the standard hydrogen electrode (f) means that copper is corroded by water itself with slow hydrogen evolution pH₂ ≈ 10⁻³ bar, i.e., H₂-gas bubbles are not seen at ambient pressure. The difference between lines (c) and (e) represents a reduction of the conventional copper immunity range. The lines (b) and (d) represent two extreme situations, with water in equilibrium with the atmospheric oxygen and hydrogen pressure, respectively.

seems also be the case for copper.¹⁷ Anyway, it is of vital importance to distinguish between O₂-free and O₂-containing water environments when discussing copper corrosion.

In Fig. 4, modified potential-pH diagram for copper is shown with supplementary data of the observed hydrogen-containing corrosion product (H_xCuO_y) inferred from the data shown in Fig. 3 and discussed above. The equilibrium of formation of this product from Cu is represented by line (e), and the close position just above the standard hydrogen electrode (f) is explained by the fact that copper is corroded by anoxic water with (slow) hydrogen evolution, pH₂ ≈ 10⁻³ bar. Hydrogen gas bubbles are definitely not seen at normal atmospheric pressure. The range between the (c) and (e) equilibria represents a reduction of the conventional copper immunity range. The lines (b) and (d) represent two extreme situations: one with water in equilibrium with equilibrated air and the other with water in equilibrium with an anoxic atmosphere with pH₂ = 5 × 10⁻⁷ bar.⁶ The extremes (b) and (d) cover most of the environments regarding dissolved molecular oxygen and hydrogen that may occur in applications where copper is in contact with water. The main consequence of Fig. 4 is that copper is not thermodynamically immune in pure water unless there is an applied hydrogen pressure in the mbar range. Native copper is nevertheless found in nature in a few locations.¹⁸ This is an indication that the hydrogen activity is “unusually” high at those geological positions or that the water (and oxygen) supply has been very restricted under geological time periods.

In most cases copper will react with water, and solid corrosion products are formed in accordance with the following schematic copper-water reaction



The formed H_{ads} in the reaction is initially atomic. Apart from hydrogen in the solid product, a fraction of atomic hydrogen is recombined to H₂ molecules and another fraction of atomic hydrogen enters the metal bulk.¹⁹ If the molecular hydrogen is removed or eliminated, the copper corrosion continues and is not automitigating, as would be the ultimate result in a fully closed system. The thermodynamic equilibrium pressure of hydrogen in air (10⁻⁴² bar) is many orders of magnitude lower than required to mitigate copper corrosion by water. Actually, any confined system with slow or limited gas exchange with the atmosphere is predicted to have a hydrogen pressure lower than in the ambient air (5 × 10⁻⁷ bar) due to surface catalysis on natural materials.⁶ The enclosure depicted in Fig. 5 is approximated to be permeable for hydrogen but not for oxygen, as most materials are more permeable for hydrogen than for oxygen. The dissolved molecular hydrogen from copper corrosion can hence diffuse through the enclosure and ultimately be consumed according to the catalyzed reaction 2H_{ads} + O_{ads} → H₂O.⁶ As the excess hydrogen is removed by external catalysis on the outer surface/

vicinity of the enclosure, a driving force for copper corrosion is maintained by an externally driven oxidation of hydrogen.

It may seem somewhat surprising that copper corrosion with hydrogen evolution in anoxic and deionized water is not observed. This is explained by: (i) the delay for the transition from O₂-consuming to hydrogen-evolving copper corrosion; (ii) the slow hydrogen-evolving corrosion with no visible hydrogen bubbles, only dissolved H₂; (iii) the low equilibrium H₂-pressure in the copper-water Reaction 1; and (iv) the fact that the anoxic corrosion product is normally only characterized with nonhydrogen-sensitive methods.

Finally, copper corrosion is a critical issue at most accelerators because they are routinely cooled by deionized and deaerated water.²⁰ The authors in this reference concluded that it is not possible to avoid solid copper corrosion products, even in those controlled systems. Only by improved filtration has the solid product accumulation been reduced to manageable rates.²⁰

Conclusion

Experiments measuring H₂-evolving corrosion of OFHC copper in deionized water were performed with additional, independent weight gain measurements. All results indicate a transition from O₂-consuming to H₂-evolving corrosion of OFHC copper in deionized water and a durability of copper in O₂-free water being determined by the hydrogen removal from the corroding surface and not by a thermodynamic immunity. Thermodynamic data describing

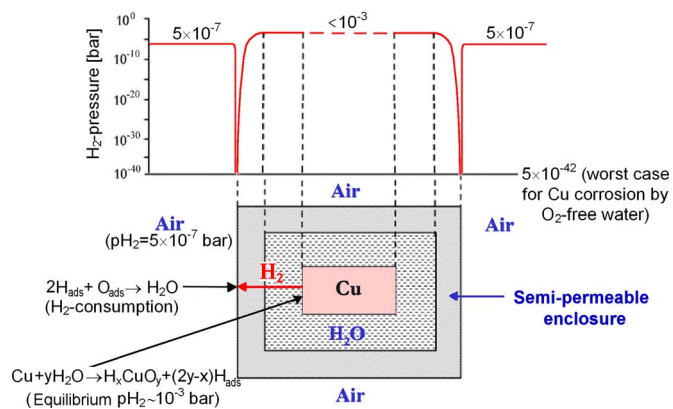


Figure 5. (Color online) Schematic representation of the impact on copper corrosion of an externally driven oxidation of hydrogen. The enclosure is permeable for hydrogen but not for oxygen. Hydrogen from the copper corrosion can hence diffuse through the enclosure and ultimately be consumed according to the catalyzed reaction 2H_{ads} + O_{ads} → H₂O.⁶ Thereby a driving force for hydrogen-evolving copper corrosion can be maintained (see text).

copper corrosion in water tend to overlook the formation of a hydrogen-containing corrosion product (H_xCuO_y). Experimental results of copper corrosion in O_2 -free water and our calculation of hydrogen concentration in equilibrated air indicate that copper corrodes at a detectable rate in contact with water, unless a hydrogen pressure in the mbar range is applied. A prerequisite for a reliable forecast of copper corrosion rates in anoxic water should hence be based on assessment of hydrogen removal by transport and catalyzed oxidation.

Acknowledgment

Lars Göthe, University of Stockholm, is acknowledged for performing the XRD measurements.

Szakalos Material Science assisted in meeting the publication costs of this article.

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