Corrosion of copper in pure O₂-free water?

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ABSTRACT

Copper exposed to pure, O₂-free water for several months in glass- and metal-contained, well-controlled systems shows no evidence of corrosion, either through hydrogen evolution or through the occurrence of oxidized copper. The results contradict the interpretation of recent experiments where it has been claimed that copper corrodes in pure, O₂-free water far above the very limited extent predicted by established thermodynamic data. Reasons for the different experimental outcomes are discussed. Experimental and theoretical efforts to identify hitherto unknown, potentially corrosion driving species of the Cu-O-H system and studies of copper/water surface reactions are reviewed as background for the present study.

1. Introduction

According to established thermodynamic data, copper is expected to corrode to a very limited extent in a closed system containing only copper and pure O₂-free water, see e.g. Refs. [1–4] and Appendix A. This is an important underlying reason for considering copper as a container material for high level nuclear waste (spent fuel) in geological repositories in e.g. Canada, Switzerland, Finland and Sweden. Since 2007, this view of the corrosion behaviour of copper has been challenged by a group of researchers [5–8], while the concern was originally raised in 1986 [9] and was also contested at that time [10,11]. One important basis for the claims of the authors of [5–8] is the observation of hydrogen gas evolution in their experiments with metallic copper in pure water. The authors have interpreted the hydrogen evolution as evidence for copper corrosion, but have not presented any explanation that is consistent with established thermodynamic data of the amount of hydrogen gas formed, or of the alleged equilibrium pressures attained in the experiments. Their setup consists of a lower and an upper stainless steel chamber connected through a palladium foil, which allows permeation of hydrogen, but no other gases, between the chambers. Metallic copper is immersed in water in a glass beaker in the lower chamber. The upper chamber is initially evacuated and the increase in gas pressure is monitored in this chamber. Similar results obtained with a similar setup were reported by Becker et al. [12].

One potential problem with these experiments concerns the stainless steel used for the setups, as all stainless steel qualities release

hydrogen gas to some extent [13]. Another complication stems from the palladium foil that can act as a sink for hydrogen by absorbing it and also by catalysing the formation of water from traces of oxygen in the system and hydrogen. A number of further concerns regarding the experiments and the interpretations in Ref. [8] have recently been discussed in this journal [14–16].

In this paper we i) give an account of the theoretical background to corrosion of copper in pure, O₂-free water, ii) present results from an alternative, comparatively simple and fast method of monitoring hydrogen evolution from copper samples in O₂-free water in glass tubes, hereby avoiding some of the difficulties we see with the set-up used in Refs. [5–8], most notably the release of hydrogen from stainless steel, iii) present results from a setup based on that used in Refs. [5–8], but for which efforts have been made to better control the experimental conditions and iv) comment on some references related to our results.

Another, and more direct, piece of evidence of copper corrosion would be the observation of oxidized copper accompanying any hydrogen evolution potentially arising from a corrosion reaction. In a parallel work [17], using a similar metal-contained well-controlled system as in iii) above, the surfaces of copper samples exposed to pure O₂-free water for up to 29 months were thoroughly examined for corrosion products as were other surfaces in the system and the water in which the copper samples were submerged. Special care was applied to the surface purity of the copper, checked by electron spectroscopy before and after the exposure to water. Results from that study are cited in the discussion section of the present paper.

As a final introductory remark, it is emphasized that the purpose of

the work presented in this paper was to examine the substance of the claims in Refs. [5–8], where the established view of copper corrosion in pure water is challenged. The approach was essentially to repeat the experiments in Refs. [5–8] under more controlled conditions and to carry out studies also with an alternative method, in both cases with most focus on hydrogen evolution. The experiments had to be designed such that they could determine the levels of hydrogen evolution rates and equilibrium pressures observed in Refs. [5–8]. The purpose was *not* to quantitatively verify the very low extent of copper corrosion in pure water predicted by the established view of copper corrosion. Such an undertaking would require a much more sensitive and differently designed experiment.

2. Theoretical background

According to established thermodynamic data, the equilibrium pressure of $H_2(g)$ in a closed system with only $Cu(s)$ and $H_2O(l)$ present initially is calculated to be of the order of 10^{-6} mbar at room temperature, when all known solid and soluble compounds of the Cu-O-H system are taken into account. The reaction that dominates the thermodynamic equilibrium is the one-electron oxidation of copper by solvated protons from the auto-ionization of water; $Cu(cr) + H^+ \rightleftarrows Cu^+(aq) + \frac{1}{2} H_2(aq)$. Several additional reactions take part in the equilibrium and the detailed equilibrium composition may be calculated using, for example, the PhreeqC software [18], see further the Appendix A. The calculated equilibrium concentration of $Cu^+(aq)$ is of the order of 10^{-12} M, while that of $Cu^{2+}(aq)$ is of the order of 10^{-17} M. This concentration ratio reflects that the disproportionation equilibrium $2\,Cu^+ \rightleftarrows Cu^{2+} + Cu^0$ is heavily displaced to the left at low concentrations; a total concentration $[Cu]_{tot} = [Cu^+] + [Cu^{2+}]$ of about 10^{-5} M is required for Cu^{2+} to become the dominating species in solution. It is emphasized that a partial H_2 pressure of 10^{-6} mbar is too small to be measurable in any of the experiments discussed in this paper. As will be discussed further below, it would also be overshadowed by the potential releases of H_2 from surface reactions.

The authors of Ref. [5] have suggested that the hydrogen pressures of up to around 1 mbar observed in their experiment may be explained by corrosion of copper by water if a hitherto unknown phase of Cu-O-H exists, which would be the thermodynamic driving force necessary for corrosion, see Fig. 4 in Ref. [5]. Recently, theoretical and experimental efforts have been made to investigate whether such a stable, but previously unknown Cu-O-H compound might in fact exist. Korzhavyi et al. [19], followed by Li et al. [20], made thorough computational investigations of the configurational space of solid CuOH using periodic density functional theory (DFT). Their results show that solid CuOH is thermodynamically unstable with respect to Cu_2O and water (and, thus, also to metallic copper and water). Soroka et al. [21] could synthesize cuprous hydroxide via reduction of Cu^{2+} ions by an Fe^{2+} salt in an alkaline (NaOH) solution. Characterization by X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infra-red spectroscopy (FTIR) suggested that the product was most likely in a hydrated form such as $CuOH \cdot H_2O$. They also showed that the compound was unstable and decomposed to a mixture of metallic copper and cuprite (Cu_2O) when heated. Cuprous hydroxide may persist as a metastable (kinetically stable) compound, but due to its thermodynamic instability with respect to copper and water it cannot be the product of sustained corrosion of copper in water. There is, thus, yet no valid support for the existence of a hitherto unknown Cu-O-H compound that has the thermodynamic properties required to drive a corrosion reaction between copper and pure O_2-free water.

It has been pointed out that surface reactivity at the copper-water interface could possibly contribute to the observed hydrogen evolution to an extent that exceeds the equilibrium pressure [22,23]. States of adsorbed OH_{ad} have indeed been observed on copper (and other metals) surfaces exposed to water [17,24–29]. Since the dissociative adsorption of water results in atomic hydrogen adsorbed on the copper

surface (H_{ad}), it is possible that hydrogen gas (H_2) could evolve for example via recombination of H_{ad} atoms (Tafel mechanism). This hypothesis is supported by gas-phase experiments, which have shown that even at a hydrogen pressure of 1 bar a polycrystalline copper surface adsorbs virtually no hydrogen [22,30–32], meaning that the desorption of hydrogen gas from copper must be a thermodynamically spontaneous (exergonic) process. In some of the experiments discussed here, e.g. in Refs. [5–8], the copper surfaces must have been covered with an oxide film with a thickness of at least a few nm. Dissociation of adsorbed water has been observed also on copper terminated $Cu_2O(100)$ and $Cu_2O(111)$ surfaces, however, there it is not clear whether the resulting hydrogen atoms stay adsorbed or if they leave the surface by forming hydrogen gas [33,34]. Other surfaces of Cu [35–37] seem to be less reactive with water. Irrespective of whether the surface consists of metallic Cu or Cu_2O, it seems clear that the water-cleaving and hydrogen-forming surface reactions proceed until at most 50 percent of a monolayer of OH_{ad} is formed, which corresponds to less than one nmol H_2/cm^2 macroscopic Cu/Cu_2O surface area. In an experimental setup like the one used in Refs. [5–8] (typically 140 cm^2 copper surface and 120 ml gas volume), this would yield a pressure of roughly 30 µbar, thus two orders of magnitude below the mbar pressures observed in that experiment. Although surface defects such as adatoms and steps can alter the energetics for the formation of OH_{ad} locally at the defect site, they cannot drive the reaction much further than on the ideal surface, since the defects are consumed by the reaction, i.e., they react by stoichiometric consumption, but do not catalyse the reaction. Surface roughness must be taken into account when discussing contributions of surface reactions to the observed amounts of hydrogen gas (and, thus, the partial pressure of hydrogen), since a rough surface has a larger effective area than a perfect surface. However, it seems unlikely that the roughness of polished copper surfaces exceeds the ideal surface area with a factor of 2 [38]. Thus, even when accounting for surface roughness, surface reactivity alone cannot explain the hydrogen partial pressures of up to one mbar reported in Refs. [5–8].

In summary, based on established thermodynamic data, equilibrium pressures in the order of 10^{-6} mbar are expected from bulk reactions of copper immersed in pure O_2-free water. From copper or cuprite surfaces immersed in water, hydrogen generation of the order of nmoles/cm^2 could be expected. In contrast, the authors of Refs. [5–8] report hydrogen partial pressures up to 1 mbar and total amounts of H_2 corresponding to hundreds of nmoles H_2/cm^2 Cu in their experiments, when including the hydrogen that leaves the system at evacuations.

It is, furthermore, erroneous to use the existence of reactions involving only the pristine copper surface atom layer as indications of the existence of stoichiometric reactions of the bulk metal. This point was further developed in Ref. [14] when discussing the example of this misconception in Ref. [8] that quotes computational surface studies reported in Refs. [6,39]. This, and other issues regarding [6], has also been pointed out in Ref. [40].

3. Experimental

3.1. Glass-contained system

The glass tube contained system for determination of hydrogen evolution from copper immersed in water was developed at Microbial Analytics Sweden AB, (Micans), Gothenburg, Sweden. The method is described in detail in Ref. [41], and details of the measurements with this method that are discussed and interpreted in the present paper are reported in Ref. [42].

When applying this method, typically two $10 \times 1\ cm^2$ copper pieces of thickness 0.2 cm or foils of thickness 0.025 or 0.05 cm were placed in a borosilicate test tube (Bellco 2048–18150) and immersed in 16 cm^3 of pure O_2-free water (20 cm^3 for the foils), leaving in both cases 6 cm^3 of gas phase above the water, see Fig. 1. The tubes were sealed with butyl rubber stoppers (1.4 cm diameter, 1.4 cm length, Bellco 2048–117800).

Fig. 1. Pairs of copper pieces immersed in pure water, contained in butyl rubber sealed borosilicate glass tubes. The 6 cm^3 gas phase at the top is sampled and analysed at regular intervals. Two tubes contain only water and gas. The image was taken after 27 months of exposure to pure, oxygen-free water at 70 °C.

The preparation of the tubes was carried out in an N_2 atmosphere in a glove box, and the tubes were stored in an N_2 atmosphere throughout the experiment. The gas phase in the tubes was sampled by inserting a syringe through the stopper and extracting 0.05 or 0.1 cm^3 of the gas phase. This was done initially and then at intervals of typically a few weeks. The gas samples were injected into a gas chromatograph in which the molar amount of H_2 was determined in each sample, after calibration of the chromatograph with standard gas mixtures. This amount was translated into a partial pressure in the tube using the known volumes of the gas phase in the tube and of the extracted gas. The following characteristics of the method are noted [41]:

– The background hydrogen partial pressure in the filled test tubes is initially very low and increases within typically a month to at most around 0.2 mbar (the dashed curve in Fig. 3, see Section 4.1). It is noted that this is well below the partial pressures of around 1 mbar for copper in pure water claimed to be caused by the establishment of chemical equilibrium in references [5–8].
– The oxidation of one monolayer of copper to Cu_2O in this setup would correspond to a pressure increase of around 0.2 mbar, assuming an ideal copper surface. Since this pressure is comparable to the background, the method is just able to detect oxidation of a single layer of copper atoms.
– A sealed test tube with 21 cm^3 water, no copper, and a controlled initial hydrogen partial pressure in the 6 cm^3 gas phase will lose hydrogen by diffusion through the butyl rubber stopper such that the partial pressure is reduced to half the initial value in about 80 days. For the same reason, a constant hydrogen generation rate from a source in the test tube causes an increasing hydrogen pressure that levels off in around 100 days [43]. At that time, the hydrogen generation is balanced by out diffusion through the stoppers. The time at which this occurs is independent of the hydrogen generation rate, while the steady state pressure level is directly proportional to it. These calculation results [43] are in agreement with loss rates of hydrogen from tubes containing only H_2 and N_2 (no water or Cu) [41].
– The accuracy in the obtained partial pressure data is about ± 15%. The experimental errors are primarily due to uncertainties in the gas chromatographic determination of the hydrogen content of the gas samples.

3.2. Metal-contained system

Fig. 2 shows the metal-contained setup with its lower and upper stainless steel chambers and the Pd foil separating them. The setup was kept in a glove box with an N_2 atmosphere. The lower chamber contains a borosilicate glass beaker (Duran) with ten 10×1 cm^2 copper foils immersed in water of ppt quality and dissolved gases were removed through bubbling with high purity nitrogen ($> 99.9999\%$ N_2). The lower chamber was loaded in the glove box with an N_2 atmosphere, which ensured that the initial oxygen content in the gas phase of the lower chamber was less than the detection limit of 0.1 ppm. In an early version of the setup, outgassing of hydrogen from the stainless steel and also from the pressure gauges caused a too high background rate in all measurements, and significant amounts of hydrogen could escape from the system through the edge of the Pd foil [44]. Therefore, two setups with improved design were developed. In these, the upper and lower 304L SS stainless steel chambers, and the 316L SS lid of the lower chamber were extensively baked out. The wall thicknesses of these components were reduced to facilitate the bake-out. The re-designed Pd
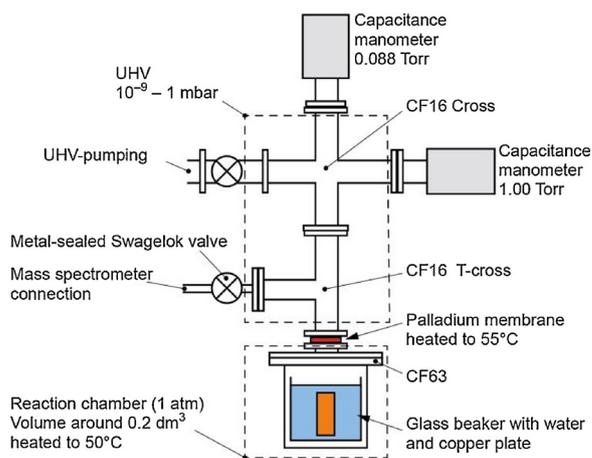

Fig. 2. Schematic view of the metal-contained setup at Uppsala University. The reaction chamber is located within the lower dashed rectangle. The tubing within the upper, dashed rectangle constitutes the upper, initially evacuated chamber.

Table 1

The glass-contained system used various combinations of copper qualities and sample preparations as shown by the shaded cells of the table.

	Alfa Aesar 99.9999% Cu-OF	Alfa Aesar 99.9% Cu-OF	Goodfellow 99.95% Cu-OF	SKB 99.95% Cu-OFP
Method I				*
Method I + SiC scratching	*			
Method II	†			*
Method II + heating to 400 °C in vacuum				
Only SiC polishing				
Only heating to 400 °C in vacuum				
None ("As received")				

*These combinations were repeated in a second run.

†This sample was not polished with SiC since it was too thin.

connections were completely tight and the previously used Baratron 627 B pressure gauges (MKS Instruments) with Inconel membranes were exchanged to Pfeiffer CCR 374 gauges with ceramic membranes that were found to have a considerably lower rate of outgassing [45]. The void volumes of the upper and lower chambers were 100 cm^3 and 250 cm^3, respectively, and the void volumes of the lower chambers are reduced to 120 cm^3 when loaded with copper foils immersed in 100 cm^3 of ultrapure water in the glass beaker. The two new setups are denoted *Setup A* and *Setup B*. *Setup A* was baked in UHV, at 440 °C for 21 days. *Setup B* was baked in air at 400 °C for four days to oxidize the surface of the stainless steel; the high temperature is expected to reduce the hydrogen content. The oxide surface layer is also expected to increase in thickness, which should reduce the outgassing from the bulk of the steel [46]. This method did, however, not give a sufficiently low outgassing rate and an additional baking was therefore performed at 300 °C for 240 h in UHV [45].

An additional *Setup C*, with identical design but less thoroughly baked out (at 150 °C), with Baratron 627 B pressure gauges and not kept in a glove box, was used for test purposes.

The setups used at Uppsala university were thus similar to those in Refs. [5–8], but there are also noteworthy differences in that the Uppsala setups have clearly described bake-out procedures, carefully measured background rates of hydrogen evolution (see below), oxygen-free conditions already initially and copper with a well determined low hydrogen content and clean, controlled surfaces as characterised by XPS and Auger electron spectroscopy (AES).

3.3. Copper samples

Four copper qualities were studied: *i*) "ultra-pure" 99.9999% Cu-OF (oxygen free) 0.025 and 0.05 cm foils (Alfa Aesar), *ii*) 99.9% Cu-OF 0.025 cm foil (Alfa Aesar), *iii*) 99.95% Cu-OF 0.01 cm foil, temper: hard (Goodfellow), *i.e.* the same copper quality as used in the long-term experiment reported in Refs. [6–8], and *iv*) 99.95% Cu-OFP (oxygen free, phosphorous doped) machined into $0.2 \times 1 \times 10$ cm^3 pieces from larger parts from SKB's canister laboratory (original material supplier: Norddeutsche Affinerie AG). The latter is the copper material intended to be used in SKB's copper canisters for final disposal of spent nuclear fuel.

Two basic sample preparation methods were applied. In the first one, denoted *Method I* and carried out at Uppsala University, electropolishing with phosphoric acid was followed by reduction of resulting oxide contaminants in a 300 °C H$_2$ atmosphere for 1 h and finally heating to 400 °C in vacuum for 2 h to bake out any remaining hydrogen [44]. The surface was subsequently characterised with XPS and AES demonstrating that it was free from oxides [17]. The surfaces of these samples were in some cases subsequently scratched with silicon carbide paper (SiC, Struers, 320 grit size − 40 μm), or with diamond powder (Diamantprofil AB, type MB-1-UM, 30 mesh), in both cases in an N$_2$ environment. The latter steps were made to modify the

topography of an ultra-pure copper surface with the purpose of making the outermost layers of copper atoms more reactive.

In the second one, denoted *Method II* and carried out at Microbial Analytics, polishing with SiC in oxic environment was followed by ultrasonic cleaning, sulfamic acid pickling and rinsing with anoxic water, all in an N$_2$ environment [41] and according to ISO 8407:2009 "*Corrosion of metals and alloys – Removal of corrosion products from corrosion test specimens*". These samples were in some cases subsequently heated to 400 °C in vacuum for about 3 h using the same equipment as in the final heating step of the sample preparation according to *Method I* described above.

Samples were also prepared by only heating to 400 °C in vacuum (no surface treatment), by SiC polishing only, and some samples were studied directly as received from the supplier. The latter was the case also for the 99.95% Cu-OF samples studied in the long-term experiment reported in Refs. [6–8]. Additional cases with Cu-OFP of less relevance for the present paper are also reported in Refs. [41].

A set of combinations of copper qualities and sample preparations was studied in the glass-contained system, given as shaded cells in Table 1. Two test tubes, each with two copper pieces, were set up for each combination and run in parallel. The two parallel test tubes yielded similar results in all cases and for simplicity, in most cases only the results from one of each parallel is displayed in the results section. Some combinations were studied in repeated experiments, again as two parallel setups.

Samples were heat treated, as part of *Method I* or as an additional step according to Table 1, in a silica glass tube in an UHV system at Uppsala University. The escaping gases were monitored with a quadrupole mass spectrometer (QMS).

In the metal-contained system, only 99.9999% Cu-OF samples prepared according to *Method I* were studied. Some of these were scratched with SiC or diamond powder before being immersed in water.

4. Results

4.1. Glass-contained system; Cu-OF 99.95% (Goodfellow)

Fig. 3 shows the observed hydrogen partial pressure in the gas phase above all sample types of 99.95% Cu-OF in the glass-contained system, along with a typical background level in those setups. None of the Cu-OF samples yields hydrogen pressures significantly above the background. The same copper quality from the same supplier was used in the long-term experiment reported in Refs. [6–8] according to our understanding. According to Ref. [6], the samples were used "as received", *i.e.* no surface treatment was conducted prior to the experiment. Therefore, the "as received" sample in Fig. 3 should be similar to that used in Refs. [6–8].

The hydrogen evolution observed in Refs. [6–8], if interpreted and expressed as a molar generation rate per unit surface area of copper, would yield a continuous pressure increase of a magnitude that is not at
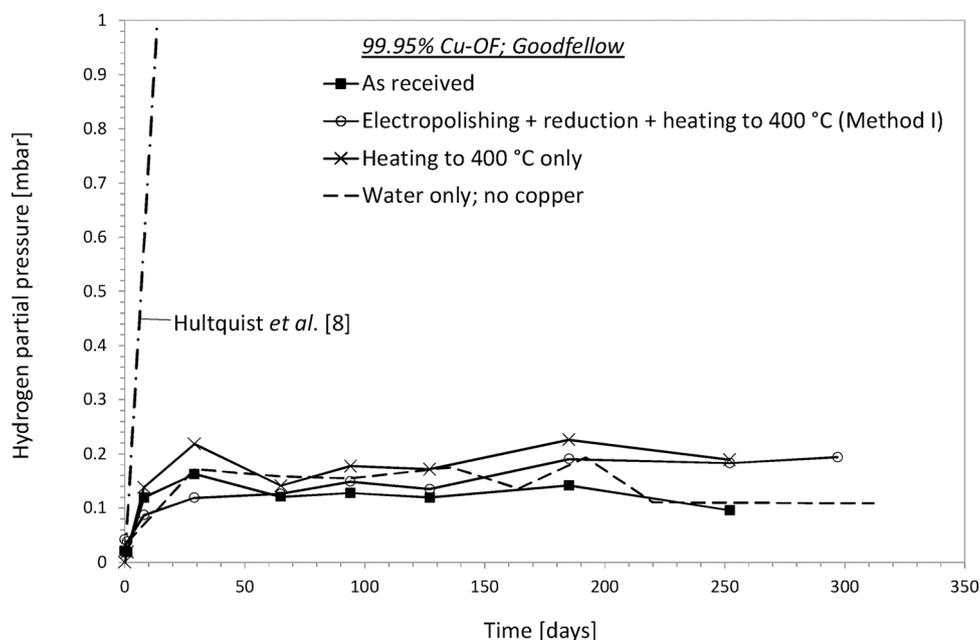
Fig. 3. Hydrogen evolution from samples of 99.95% Cu-OF with different surface treatments. The expected hydrogen evolution rate according to Hultquist et al. [8] is also shown. The lines serve only as guidance for the eye and do not express measured pressures between the sampling points.

all observed, as illustrated in Fig. 3. Hultquist et al. [8] report an increase of hydrogen partial pressure to a rate of 4×10^{-4} mbar/h at 52 °C with a gas volume of 120 cm^3 and a copper surface of 140 cm^2. For the conditions in the glass contained system, namely 45 cm^2 of Cu in a 6 cm^3 gas volume, this would correspond to a pressure increase of around 0.074 mbar/24 h, *i.e.* 7.4 mbar in 100 days (dashed-dotted line in Fig. 3). A signal of that magnitude would thus be readily detected in the glass contained system. According to Ref. [7] the hydrogen evolution is expected to cease at a partial pressure of around 1 mbar, i.e., a pressure that was never attained in the glass contained setup with this particular copper quality.

4.2. Glass-contained system; Cu-OF 99.9999% and 99.9% (Alfa Aesar)

The samples of 99.9999% and 99.9% Cu-OF exhibited a similar behaviour as those of 99.95% Cu-OF in Fig. 3, *i.e.,* no hydrogen evolution was observed even after hundreds of days of exposure to pure O$_2$-free water. The only exception was the case where the samples were cleaned by electropolishing (*Method I*) followed by scratching of the copper surface with SiC paper in an N$_2$ environment. Fig. 4 shows the development of both the parallel tubes in each of the two runs with the scratched samples of 99.9999% Cu-OF. An electropolished, unscratched sample is shown for comparison. The scratched samples yielded a significant initial hydrogen evolution, in particular in the first run. The development after the first data point indicates that the evolution of hydrogen gas has already ceased and the further development is consistent with an outward diffusion of the initially generated hydrogen through the butyl rubber stoppers of the test tubes used in the glass contained setup, calculated from solubility and diffusivity data for hydrogen in butyl rubber at 70 °C [47] and geometrical data for the setup [43]. To verify that the initial hydrogen generation had ceased, the gas in one of the two parallel samples was evacuated after 244 days in run 1 and after 142 days in run 2, and the subsequent pressure developments demonstrate that hydrogen did then not evolve above the background value.

SEM examination of SiC-scratched samples before exposure to water revealed trenches and loose copper particles on the surface [45]. Powder XRD examination of the copper foil after the exposure to water revealed the occurrence of the very same pattern as that yielded by the SiC paper used, indicating the presence of particles stuck in the soft

copper matrix [45]. The composition of the polishing paper particles was not analysed further. As discussed above in Section 2, both copper and copper oxide surfaces react with water to an extent that could generate up to somewhat less than one nmol H$_2$/cm^2 from an ideally flat surface. Also a flat Si-terminated SiC(001) surface may react to a similar extent [48], generating similar amounts of H$_2$. The observed amounts of H$_2$ from the scratched samples are at least an order of magnitude higher than what would be expected from perfectly flat surfaces. The roughening of the Cu surface through the SiC scratching and accompanying particles of both SiC and Cu (as observed) could increase the effective surface area of the sample considerably. Moreover, the structural defect density gets higher. It would, however, require additional investigations to clarify if the extent of area increase could correspond to the observed H$_2$ generation. Also binding agents and other constituents of the polishing paper that are likely to have contaminated the Cu surface could be involved in the H$_2$ generation.

The study of the surface effect behind the results in Fig. 4 has not been pursued any further since it is beyond the scope of the paper.

4.3. Glass contained system; 99.95% Cu-OFP

Fig. 5 shows the observed hydrogen partial pressure in the gas phase above all sample types of 99.95% Cu-OFP (SKB canister copper). This copper quality has in earlier experiments, with surface treatment according to *Method II*, yielded significant and sustained hydrogen evolution [41]. In the current experiments, this combination of copper quality and surface treatment yielded similar results as earlier, *i.e.* hydrogen evolution significantly higher than the background. The curve levels off after around 100 days and this is quantitatively consistent with a balance between the initial hydrogen production rate and out-diffusion through the stoppers in the setup, using the same diffusivity and solubility data as in the evaluation of the pressure drops for the 99.9999% Cu-OF samples shown in Fig. 4 and reported in Ref. [43]. It is also consistently found that when the gas phase of samples of this kind is evacuated once a steady pressure is reached, then a similar, albeit somewhat slower, pressure build-up as initially restarts, and this applies also for repeated evacuations [41]. This can be seen in the curve of Fig. 5 that shows the results of the sample that was SiC polished only. The similarity of the hydrogen evolutions from that sample and the one that has also been sulfamic acid pickled indicates that the acid pickling
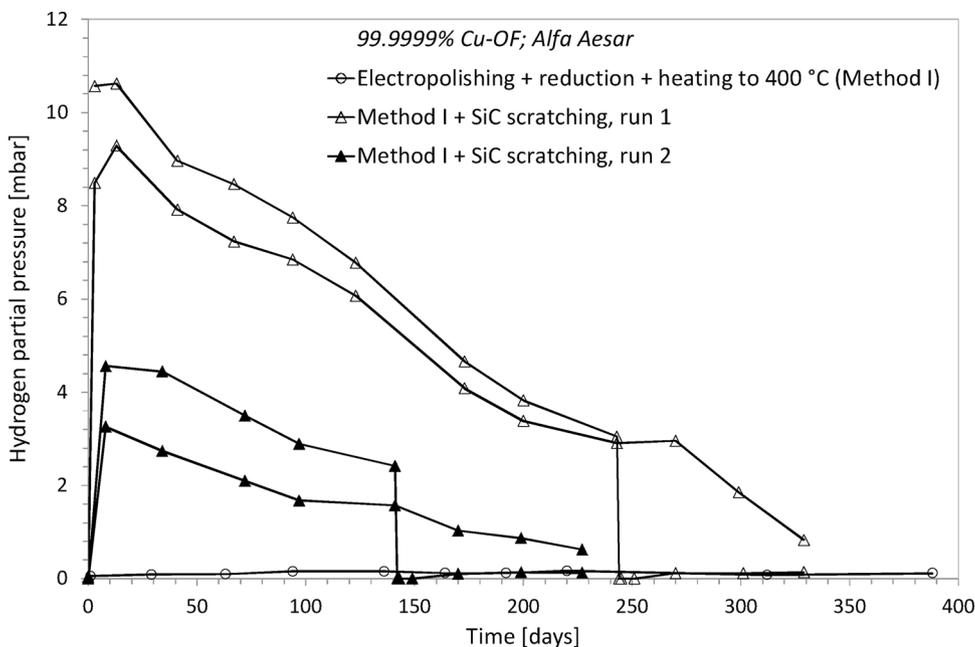
is unrelated to the cause of the hydrogen evolution.

In a preparatory test [42, Section 4.12], it was observed that the canister copper yielded hydrogen evolution also if no water was present in the test tubes, and at a rate comparable to the case where also water was present. This led to the hypothesis that the observed hydrogen gas from the Cu-OFP samples emanates from out-gassing of hydrogen present in the copper metal; 99.95% Cu-OFP contains typically 0.5 wt-ppm hydrogen [49]. Therefore, as-received samples of canister copper were heated to 400 °C in vacuum for 3 h, prior to exposure to O₂-free water, and outgassing of H₂ during heating was confirmed by mass spectroscopy. This yielded a significant change: Following a fast, initial pressure increase to almost 2 mbar, the hydrogen evolution ceased. The initial evolution may be due to reactions with impurities on the copper surface that had not been cleaned in this case. A subsequent evacuation of the hydrogen gas after 142 days demonstrated that the hydrogen

evolution had indeed ceased, Fig. 5. Samples that were surface treated according to *Method II* and subsequently heated to 400 °C in vacuum, did not exhibit any hydrogen evolution above background. If the canister copper was treated according to *Method I*, where the final step is heating to 400 °C in vacuum, a short, initial hydrogen evolution was observed in a first run, whereas a repetition of the experiment yielded no hydrogen evolution above background (both runs shown in Fig. 5). Evacuation of the hydrogen gas after 244 days in the first run confirmed that the hydrogen evolution had ceased. The reason for the initial, short term hydrogen evolution in that run is not known. It could be due to contaminations or accidental scratching from adjacent copper pieces, in both cases arising in the several steps involved in transporting the samples between Uppsala University, where the samples were prepared according to *Method I*, and Microbial Analytics AB, where they were emplaced in test tubes and exposed to water.
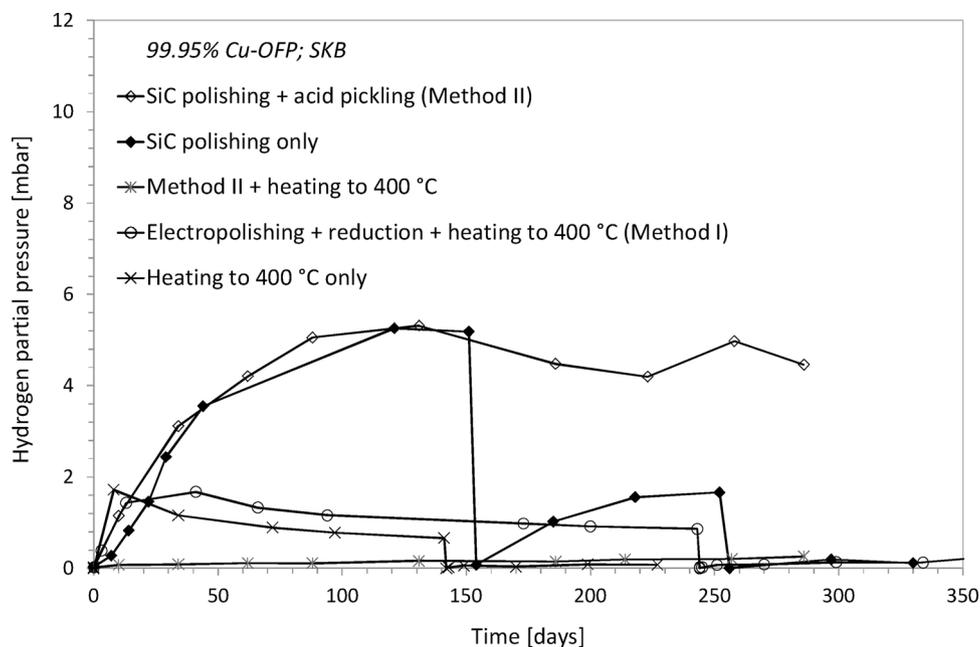

Fig. 5. Hydrogen evolution from samples of canister copper; 99.95% Cu-OFP with different surface treatments.
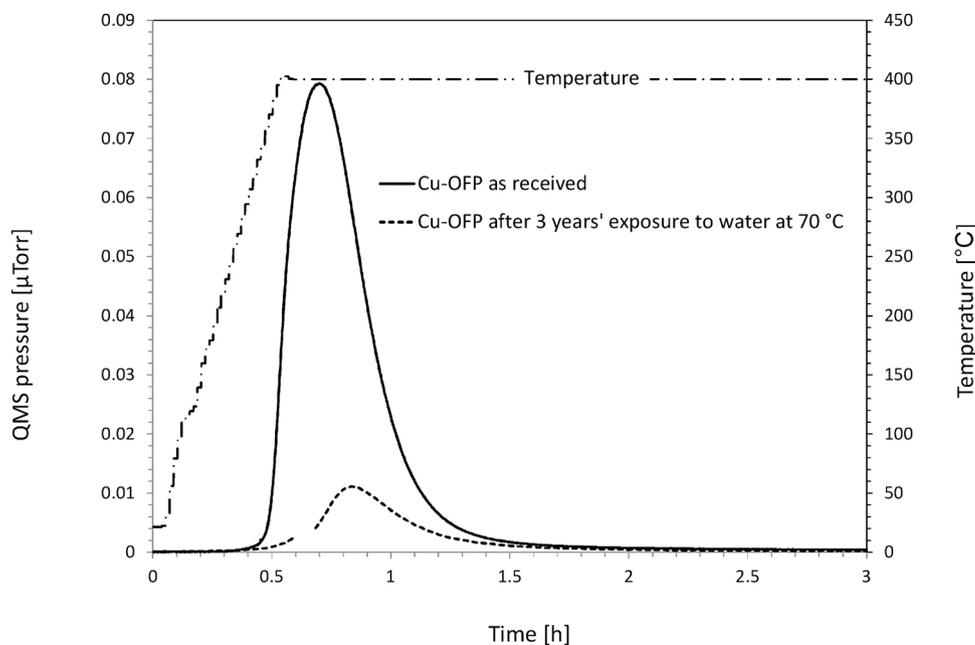
Fig. 6. Hydrogen outgassing rates when heating two copper Cu-OFP samples to 400 °C, as measured by QMS pressure. Solid line: Degassing rate when heating an "as received" sample to 400 °C, prior to exposure to water. Dashed line: Degassing rate when heating Cu-OFP sample N3:7 [42] after surface cleaning with *Method II* (i.e., no heating) and exposure to water for approximately 3 years at 70 °C. (The gap in the dashed line is due to a temporary failure of the data logging system.) Dash-dotted lines and right-hand vertical axis: Temperature.

The mentioned outgassing of hydrogen when heating a 2 mm thick 99.95% "as received" Cu-OFP sample to 400 °C is shown in Fig. 6. The figure also shows the outgassing rate of a Cu-OFP sample that has been cleaned with *Method II* and subsequently exposed to pure, O_2-free water in the glass-contained system for approximately 3 years (the N3:7 sample in Ref. [42]). This sample exhibited an initial H_2 evolution of about 3 mbar/month in the glass contained system, which had decreased to about 0.7 mbar/month after approximately 1 year [Fig. 3 and 4 in Ref. 42]. Taking the latter value as an average evolution rate over the three-year period, a total of 25 mbar of H_2 was evolved to the 6 cm^3 gas volume, corresponding to 5 µmoles of H_2 or around 10 µg H. The total copper mass in a glass tube with two Cu-OFP pieces is around 36 g. The H content evolved thus corresponds to roughly 0.3 wt-ppm, whereas a typical H content in Cu-OFP is around 0.5 wt-ppm [49]. This estimate, albeit coarse, indicates that the hydrogen evolution observed for the Cu-OFP samples in the glass contained system is consistent with the observed decrease in outgassing rates when comparing a sample exposed to 70 °C for 3 years with an unexposed sample. The 99.95% and 99.9999% Cu-OF qualities exhibited outgassing rates when heated to 400 °C that are roughly comparable to that of the 99.95% Cu-OFP, despite different manufacturing procedures and impurity levels.

It is emphasized that the extent of outgassing observed in Fig. 6 applies only to the particular Cu-OFP samples entailing a minor part of this study (see Table 1) and that these samples had a thickness of 2 mm. It is not seen as plausible that outgassing could be the explanation of e.g. the hydrogen evolution observed in Refs. [5–8,12], where other sample types (Cu-OF) and thinner foils (typically 0.1 mm) were used. Such samples have been used also in the present study and they did not yield any hydrogen evolution, as presented in preceding sections.

Regarding the nature of hydrogen in Cu-OFP, it has been demonstrated that oxygen tends to occur as phosphates in Cu-OFP rather than as oxides as in Cu-OF [50]. Possibly, copper oxides are more prone than copper phosphates to bind or react with hydrogen [50], which would result in a weaker trapping of H in Cu-OFP than in Cu-OF. Thermal Desorption Spectroscopy studies of Cu-OFP and calculations of transport of hydrogen in Cu-OFP in the presence of H traps in the material are planned to further elucidate the nature of H in Cu-OFP.

4.4. Metal-contained system

Setup A was first run at 50 °C with only water in the glass beaker in the lower chamber and then with copper foils treated with *Method I* and

scratched with diamond powder. Prior to the run that contained the copper samples, these were submerged in ultrapure water and left in the glove box for 6 days to allow the escape of any hydrogen from possible short-term reactions, similar to those observed with scratched surfaces according to the results in Section 4.2. The two runs (without and with copper, respectively) are shown in Fig. 7. As can be seen, there is no noticeable difference between the runs. The initial, approximately quadratic increase in pressure is due to the efficient absorption of hydrogen at low pressures by the palladium foil separating the two chambers. The background rate is also quantitatively consistent with the rate measured with the system empty (no glass beaker) and with no palladium foil separating the chambers [45]. Since the same background occurs also without water in the system, it cannot be due to aqueous corrosion of stainless steel. As elaborated in Ref. [45], the measured outgassing rates from the stainless steel are compatible with data reported in the literature for this material and bake-out procedure. The results with this setup are in stark contrast to the claims of hydrogen evolution being due to copper corrosion in Refs. [5–8]. It is also noted that the reported hydrogen evolution rate of 4×10^{-4} mbar/h at 52 °C in Ref. [8], a setup with similar dimensions as *Setup A*, would
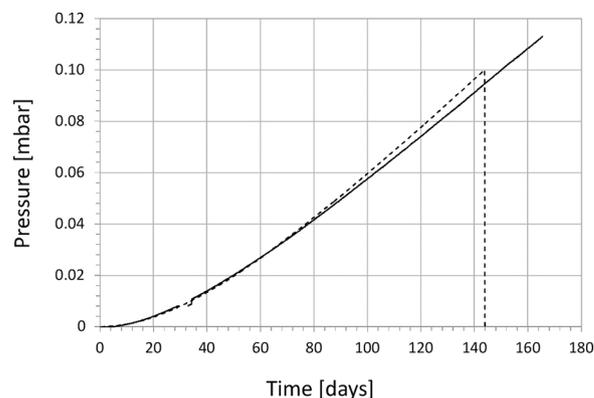

Fig. 7. Hydrogen evolution measured in Setup A at 50 °C equipped with a Pd membrane. Dashed curve: Background with only water in the lower chamber. Solid curve: Diamond scratched 99.9999% Cu-OF treated with Method I immersed in water in the lower chamber. (The irregular feature of the solid curve at around 35 days is due to an artefact from a power failure in the data logging system.).

have yielded a hydrogen partial pressure of around 1 mbar in 100 days. As for the glass contained system, such a signal would have been readily detected in this metal-contained system. This also means that the background hydrogen pressure in *Setup A* throughout the experiment was about an order of magnitude below the claimed equilibrium pressure of around 1 mbar in Refs. [5–8]. The background hydrogen would thus not have suppressed the hydrogen evolution from the corrosion reaction, in case the latter were of the extent claimed in Refs. [5–8].

Setup B was run at 50 °C with copper treated according to *Method I* and scratched with SiC, and also with copper treated with *Method I* but not subsequently scratched. Background measurements were made before, between and after the two measurements with copper. The first of the three background runs showed higher hydrogen evolution rates than the other two, and the first background rate also increased with time, indicating that the environment in the setup was not stable, at least not initially, contrary to the case with *Setup A* [45]. The reason is unclear but could be due to the bake-out procedure used for *Setup B*, which differed from that used for *Setup A*.

The SiC-scratched copper showed hydrogen evolution above background, qualitatively consistent with the corresponding samples of the glass contained system as shown in Fig. 4. Quantitative conclusions could not be drawn due to the unstable background.

The measurements in *Setup B* with copper treated with *Method I* but not subsequently scratched yielded no hydrogen evolution above the two backgrounds obtained before and after this measurement, i.e. the result was similar to that obtained with *Setup A*. However, since the background measurements in *Setup B* could not be fully explained, we are not drawing any firm conclusions from the results obtained with this setup, but note that they indicate the same absence of appreciable hydrogen evolution above background.

In the additional *Setup C*, a test of the effect of adding ≈ 0.2 mbar of O_2 gas in the lower chamber was made. It was demonstrated that this addition of oxygen caused the hydrogen pressure in the upper chamber to decrease from ≈ 0.3 mbar to ≈ 0.1 mbar, which is interpreted as a reaction of hydrogen with oxygen at the Pd surface facing the lower chamber. This demonstrates that trace amounts of oxygen in the system may complicate the interpretation of hydrogen evolution as deduced from pressure measurement: If a small amount of oxygen is present when a hydrogen background is measured, then any hydrogen evolution may be disguised until the oxygen has been consumed by catalytic water formation at the Pd membrane.

Details of the measurements with the three setups are given in Ref. [45].

5. Discussion

5.1. Summary of results with glass contained system

The results from the glass-contained system can be summarised as follows.

1. Of the studied samples, only 99.95% Cu-OFP (SKB canister copper) yielded hydrogen evolution that continued for more than a few days. This sustained evolution was not observed if the samples were heated to 400 °C in vacuum prior to the exposure to water. During heating, a substantial out-gassing of hydrogen was observed. These observations indicate that the hydrogen gas evolved in experiments with canister copper emanates from hydrogen initially present in the copper material, and that it is not due to a corrosion process. This interpretation is further supported by the observation that hydrogen evolves also in test tubes with only canister copper and no water.
2. No other combinations of treatments and copper qualities yielded hydrogen evolution that lasted for more than a few days at most. Due to the chosen gas sampling intervals, it cannot be excluded that the initial evolution was much shorter. The extent of the evolution depends on the copper quality and the surface treatment and

corresponds (theoretically), at most, to oxidation of a few layers of copper atoms.
3. A clean copper surface can be modified so that the initial hydrogen evolution increases significantly. Silicon carbide scratching in an N_2 environment of a carefully cleaned copper surface may yield hydrogen evolution up to 10 mbar, which in the experimental setup corresponds to around 50 nmol H_2/(cm^2 Cu). Also this process ceased after at most a few days.

These results give no support for the existence of a sustained corrosion of copper in pure, O_2-free water above the detection limit of the experiment. This limit is fully sufficient to detect the evolution rates claimed in Refs. [6–8].

5.2. Summary of results with metal-contained system

Also the results of the metal contained setups imply that no hydrogen evolution above background is obtained from a clean copper surface in pure, O_2-free water. This is most clearly demonstrated with *Setup A* that was the more thoroughly baked out system before the experiments. Also the results from *Setup B* indicate no influence of the presence of copper, but the initial behaviour of this setup is not fully understood.

In addition to the experiments reported above, the Uppsala group has carried out a range of measurements with copper immersed in water in glass beakers in metal contained systems where hydrogen evolution was not monitored [17]. Those experiments were aimed at examining whether any evidence of oxidized copper could be found in setups similar to those reported here, but without the upper chamber, so that any hydrogen formed (from whatever source) could escape to the surroundings through a Pd foil. The free access of hydrogen to the surrounding glove box atmosphere suggests that the deviation from thermodynamic equilibrium would increase the corrosion rate. The rate of formation of oxidized copper is a more direct probe of corrosion than the monitoring of hydrogen. The copper samples were analysed with XPS and AES, the water with inductively coupled plasma mass spectrometry (ICP-MS) and the glassware with ICP-MS (through leaching with nitric acid) and with X-ray fluorescence spectrometry (XRF). In summary, no Cu_2O was detected, i.e. less than a monolayer on the copper surfaces after exposure to pure, O_2-free water for up to 29 months. Also the amount of copper found in the water corresponds to less than a monolayer of the exposed Cu surface. Significantly less than a monolayer of Cu was found on the glass walls, although the translation of the XRF signal to an equivalent surface coverage is uncertain in this case. Moreover, fusion analysis of the copper performed before and after prolonged water exposure showed neither any loss nor accumulation from the initial low hydrogen content of 0.03 ppm. In summary, if one assumes that the oxide on the copper surface, and the copper found on the glassware and in solution all occurred as metallic copper in the Cu sample initially, the Uppsala study gives a corrosion rate of < 0.3 nm/yr.

5.3. Comments on the study reported in Ref. [12]

A brief attempt to repeat the findings in Ref. [5] was made by Becker et al. [12]. They studied, in a similar system as those used in Refs. [5–8], copper and platinum foils immersed in water in two separate runs and noted a substantially higher hydrogen evolution rate in the copper run compared to the platinum run. In that experiment, the copper or platinum containing lower chamber was loaded in air. The chamber was subsequently evacuated [12], but with about 1 mbar of O_2 remaining [52]. This oxygen is expected to quickly react with copper in the copper run whereas it is expected to be unaffected in the platinum run. The oxygen in the platinum run could thus be expected to react with any evolving hydrogen in that run, since both the platinum itself and the palladium foil separating the two chambers would act as

catalysts of such a reaction. This is the same effect as demonstrated with *Setup C* above. It is, thus, suggested that hydrogen gas was evolved also in the platinum run, but masked by the presence of oxygen. The hydrogen evolution rate in the Cu run was similar to that observed in the Uppsala experiment and it is therefore suggested that it emanates from release of hydrogen present in the stainless steel of the experimental chambers. The suggested explanation is consistent with the outgassing rates from stainless steel [53] and the influence of trace amounts of oxygen in the gas phase on hydrogen evolution rates observed in the experiments with *Setup C* by the Uppsala group.

5.4. Comments on the studies reported in Refs. [5–8]

In the blank experiment reported in Ref. [5], small amounts of O_2 remain at the onset of the measurement of H_2 evolution. Also here, this oxygen may well have reacted with hydrogen and disguised any ongoing hydrogen evolution during the blank experiment. When the experiment is run with copper present, any remaining oxygen is expected to quickly react with copper, hence leaving hydrogen unaffected.[1] The efficient absorption of hydrogen by the Pd foil constitutes an additional factor complicating the interpretation of very low hydrogen pressures involved in the background measurements. We find the account of hydrogen sources and sinks in Refs. [5–8] insufficient for an evaluation of the overall hydrogen balance in those experiments. An explanation of their observed rates of hydrogen evolution can, thus, not be offered, but it is noted that no measurement of background rates of hydrogen are reported for the setup used in Refs. [6–8] and that the hydrogen evolution rates reported are at least not inconsistent with typical outgassing rates from 316L SS stainless steel [53]. See also the discussions in Refs. [14–16]. Concerns regarding the interpretations in Ref. [5] have also been expressed and discussed in Refs. [53,54].

Solid corrosion products are claimed to have developed during a 2.2 year exposure to pure water on the Cu sample shown in Fig. 4 of Ref. [8]. Here, we note that *i)* the surface was not characterised prior to the exposure, *ii)* the water was not oxygen free at the start of the exposure, and *iii)* the sample was exposed to oxygen for 6 months between the exposure and the characterisation of the surface. Copper oxide will form on the surface to a considerable amount within minutes in air, easily detected by Auger spectroscopy. We thus cannot consider this figure as evidence of corrosion products developing on copper in O_2-free water.

5.5. Comments on additional studies

A couple of additional studies are frequently cited in the discussion of copper corrosion in pure O_2-free water and, therefore, we comment on them here.

Cleveland et al. [55] have presented a kinetic model for copper in pure water, with results suggesting even higher corrosion rates and equilibrium hydrogen partial pressures than in references [5–8]. The study was criticized [56] and the criticism was responded to [57]. A further brief contribution to the discussion was given in Ref. [14], pointing to the large discrepancy between the modelling results in [57] and established thermodynamic data, despite the fact that the Pourbaix diagrams presented in Ref. [55,57] are based on established thermodynamic data. In discussions [58] with the corresponding author of Refs. [55,57], it has been clarified that the author fully supports the basic notion that results predicted by a kinetic model should be consistent with thermodynamic data. In these discussions, the author also pointed out that kinetic data for the model were taken from other

systems than copper in pure water due to lack of literature data for the latter systems, as was also described in the first publication of the kinetic model [55]. In the discussions it was concluded that further literature studies and modelling work is required in order to clarify whether it is possible to establish a quantitative kinetic model for copper corrosion in pure, oxygen-free water.

In another work, Hultquist et al. [59] exposed copper foils to distilled water for 15 years in E-flasks. One of the flasks was sealed with a 0.1 mm hydrogen permeable Pd foil and the other with a glass stopper. UHV-glue (Varian Vacuum Technologies) was used to secure a gas tight seal. After 15 years, the difference between the copper foils in the two flasks was striking; in the glass sealed flask the copper foil still had a metallic "shine", the copper in the Pd sealed flask was all black with green spots. The water level in that flask was also noticeably lower than the starting level. The authors report a corrosion rate of 5000 nm/yr in the Pd sealed flask and claim that corrosion may proceed at a high rate without the system reaching equilibrium since hydrogen is continuously being removed.

This experiment was repeated by Ollila [60], but under more controlled conditions, in particular in that the experiment was made in a glove box with inert atmosphere and the E-flasks were kept in a stainless steel container in the glovebox. Following exposure to O_2-free water for about two years, the copper and glass surfaces and the water were analysed for one of the Pd-sealed flasks. The analyses showed an up to 6 nm thick Cu_2O layer on the Cu surface. It is, however, plausible that all of this was present from start, since the copper foils were only polished but not reduced under oxygen free conditions. In total 5.6 µg of Cu was found in the water and on the walls of the E-flasks. This amount corresponds (theoretically) to about $6 \cdot 10^{-7} \, cm^3$ Cu on 85 cm^2, i.e. about 0.07 nm Cu. The observed Cu (surface oxide, in water and on glass walls) thus corresponds to corrosion of Cu of at most 6 nm in two years, or a maximum of 3 nm/yr. This is in stark contrast to the roughly 5000 nm/yr reported in Ref. [59]. In that experiment, the flasks were stored in air. In Ref. [60] a test with a flask in air was also carried out; here the Cu surfaces were substantially altered (darkening, and green spots appearing), which was interpreted as being due to leakage of air into the E-flasks. These alterations were similar in nature to those reported in [59]. We thus suggest that an in-leakage of air caused the observed corrosion in that study. We also note that the corrosion rate reported in Ref. [59] is much higher than even the ones claimed by the same leading authors in Refs. [5–8], and without any attempt to reconcile these considerable differences in any of the publications.

5.6. General comments on metal vs glass contained systems

Several of the issues discussed in Sections 5.2–5.4 point towards problems with the experimental design of the metal-contained systems that were used in Refs. [5–8,12], and at Uppsala University, in that there are several sources and sinks of hydrogen that are difficult to quantify and control. The palladium foil used to selectively allow hydrogen to pass from the lower to the upper chamber may act as a catalyst of water formation and, particularly at low partial pressures, entails a considerable sink for hydrogen. Both these effects complicate the interpretation of data from the experiments. The stainless steel in the equipment contains and releases hydrogen that also complicates the interpretation of the results. The glass contained system does not have any of these complications, facilitating the interpretation of results obtained with this system. A disadvantage with the latter system is, however, that the slow leakage of hydrogen through the stoppers needs to be considered when interpreting the results.

In particular, the same copper quality, in the same "as received" condition as that in Refs. [6–8] did not yield any hydrogen evolution in the glass contained system. This implies that the hydrogen evolution observed in Refs. [6–8] is not due to corrosion of copper. This important example illustrates how the simpler glass contained system allows more distinct conclusions to be drawn than does the metal contained system.

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[1] Although metallic copper and water is the thermodynamic fate of a closed system of cuprite and hydrogen gas, the reduction of cuprite is slow at ambient temperatures, reflected by the fact that the apparent E_a for the reduction of cuprite by hydrogen gas is as high as 1.2 eV $\approx$ 116 kJ/mol [51].

Another distinguishing characteristic of the glass contained system is the multitude of samples that can be analysed in a relatively short time and with reasonable resources. It would not have been realistic to carry out the extensive measurement program according to Table 1 in a metal contained system. The glass contained system also exhibits a distinct response to initial, short-term releases of hydrogen, for which an example is shown in Section 4.2. The metal-contained system does not exhibit a similarly clear response due to the presence of the hydrogen-absorbing Pd foil, which contributed to the difficulties of interpreting the results from *Setup B* (Section 4.4) where the SiC scratched sample could have released a short-term pulse of hydrogen similar to that observed in the glass contained system (Section 4.2).

5.7. Significance for copper as a container material for geological disposal of radioactive waste

The results presented in this paper do not support recent claims [5–8] of copper corrosion in pure O_2-free water occurring to an extent that exceeds that predicted by established thermodynamic data. There is, hence, no reason to include such a phenomenon in the scientific basis for safety assessments of nuclear waste repositories. It is, nevertheless, noteworthy that the rate of hydrogen evolution reported at room temperature in Reference 8, would, if interpreted as a signature of copper corrosion, correspond to a corrosion rate of about 5 nm/yr, see [14] for further details. This translates into 5 mm in 10^6 years, a time frame often used for safety assessments of repositories for high-level nuclear waste. With a copper container thickness of e.g. 5 cm there is thus a considerable margin for corrosion failure even in the time perspective of 10^6 years, and even if the observed hydrogen evolution were interpreted as due to copper corrosion. For an in-depth discussion of corrosion phenomena of significance in the geological environment of granitic rock, see Ref. [61].

6. Conclusions

The experimental work presented in this paper was undertaken to evaluate claims in Refs. [5–8] that copper corrodes in pure, O_2-free water to an extent far above that predicted by established thermodynamic data. The sensitivities of the experiments were fully sufficient to detect the signals observed in Ref. [5–8]. No such signals that could be related to copper corrosion were observed. In particular, the following findings emerged.

i No hydrogen evolution above the experimental background was observed from copper immersed in pure O_2-free water in the glass

contained system, for a range of copper qualities and surface treatments. The only example of a continuing hydrogen evolution was due to outgassing from that particular copper quality.

ii No hydrogen evolution above the experimental background was observed from copper immersed in pure O_2-free water in the run with *Setup A* among the metal contained systems. The results from *Setup B* support this conclusion but are seen as weaker due to the unstable behaviour of the setup in the initial stages of the run.

The findings from the metal contained systems are further strengthened by the absence of corrosion products in the long-term studies up to 29 months in similar setups reported elsewhere [17].

The theoretical background given in this paper demonstrates that, despite recent efforts, no hitherto unknown, stable Cu-O-H compound has been found that could act as the thermodynamic driving force of a continuing corrosion reaction in pure, O_2-free water, contrary to the claims in Ref. [5].

We have also discussed possible explanations, other than copper corrosion, of the observations of hydrogen evolution in Refs. [5–8] and also in Ref. [12].

In summary, the results presented in this paper give no support for the existence of a sustained corrosion of copper in pure, O_2-free water at an extent above the sensitivities of the experimental methods used. In particular, the extent of hydrogen evolution, interpreted as evidence of copper corrosion in Refs. [5–8], would have been detectable. The lack of observed signals is consistent with the notion that such corrosion occurs only to the very limited extent predicted by established thermodynamic data. We have, however, not quantitatively verified this very limited extent. Such an undertaking would require a much more sensitive and differently designed experiment.

Appendix A. The thermodynamics of copper in pure, O_2-free water

The final state of a system consisting initially of metallic copper immersed in pure, O_2-free water at 298 K calculated with the publicly available PhreeqC open source software [18] is given in Table A1. The calculation considers all known species of the Cu-O-H system. The evolution of the system is dominated by the reaction

$$Cu(cr) + H^+ \rightleftarrows Cu^+(aq) + \tfrac{1}{2} H_2(aq) \tag{1}$$

and, to a much lesser extent, by

Table A1

Equilibrium activities and partial pressure of H_2 at 298 K calculated manually with data from Table A2 and with the PhreeqC software using the databases included in the PhreeqC software distribution (file "minteq.v 4.dat" for all species, except the values for $H_2(g)$ which were from file "phreeqc.dat"). The PhreeqC databases cover all known species of the Cu-O-H system. Species with calculated activities down to 10^{-18} M are included in the table.

Species	PhreeqC	Manual calculation	Species	PhreeqC	Manual calculation
$\{Cu^+\}$	$3.52 \cdot 10^{-12}$ M	$3.4 \cdot 10^{-12}$ M	$\{H_2(aq)\}$	$1.77 \cdot 10^{-12}$ M	$1.7 \cdot 10^{-12}$ M
$\{Cu^{2+}\}$	$1.45 \cdot 10^{-17}$ M	$1.5 \cdot 10^{-17}$ M	$\{H^+\}$	$1.00 \cdot 10^{-7}$ M	$1.00 \cdot 10^{-7}$ M
$\{CuOH^+\}$	$4.58 \cdot 10^{-18}$ M	–		$2.3 \cdot 10^{-9}$ bar	$2.1 \cdot 10^{-9}$ bar
			p_{H_2}		

Table A2

Values of Gibbs free energy of formation, ΔG_f^0 in kJ/mol, at 298 K from [63]. The standard state for pure liquid or solid substances is the pure substance at the standard state pressure of 1 bar, while for aqueous species the standard state is a hypothetical ideal solution, at the standard state pressure of 1 bar, in which the concentration of the solute is 1 mol kg^{-1}, and in which the activity coefficient of the solute is unity.

Species	ΔG_f^0	Species	ΔG_f^0
Cu(cr)	0	H$^+$	0
Cu$^+$	50.3	H$_2$(g)	0
Cu^{2+}	65.7	H$_2$(aq)	17.6

$$2Cu^+ \rightleftarrows Cu^{2+} + Cu(cr) \tag{2}$$

By considering also the equilibrium

$$H_2(g) \rightleftarrows H_2(aq) \tag{3}$$

the partial pressure of hydrogen, p_{H_2}, is obtained.

The fact that (1) is the main reaction may be seen by manually calculating the equilibrium for this reaction from the thermodynamic data from Ref. [62] given in Table A2. The equilibrium constant of reaction (1), K_1, is obtained as

$$K_1 = \exp\left(-\frac{\sum \Delta G_{f,products}^0 - \sum \Delta G_{f,reactants}^0}{RT}\right) \tag{4}$$

Here

$$\sum \Delta G_{f,products}^0 = \Delta G_{f,Cu^+(aq)}^0 + \frac{1}{2}\Delta G_{f,H_2(aq)}^0$$

and

$$\sum \Delta G_{f,reactants}^0 = \Delta G_{f,H^+}^0 + \Delta G_{f,Cu(cr)}^0$$

R is the molar gas constant and T is the absolute temperature. With data from Table A2 one obtains $K_1 \approx 4.4 \cdot 10^{-11}$ for $T = 298$ K.

The constants K_2 and K_3 for Reaction (2) and (3) are similarly obtained as $1.3 \cdot 10^7$ and $8.25 \cdot 10^{-4}$, respectively. Applying K_1 to reaction (1), and assuming zero activities of the products initially, yields the manually calculated final activities of Cu$^+$ and H$_2$(aq) according to Table A1. At these low concentrations, only a minute fraction of Cu$^+$ will disproportionate to Cu(cr) and Cu^{2+} as governed by Reaction (2), yielding the very low activity of Cu^{2+} given in Table A1. Reaction (3) yields the equilibrium partial pressure of H$_2$ from the activity of H$_2$(aq) when there is no gas volume in the system. Both the PhreeqC and the manually calculated results are in good agreement with the calculations reported in [62].

To demonstrate the impact of a gas volume in the system, Reactions (1) and (3) can be combined into

$$Cu(cr) + H^+ \rightleftarrows Cu^+(aq) + \tfrac{1}{2}(1-a)H_2(aq) + \tfrac{1}{2}a\,H_2(g) \tag{4}$$

where a is the proportion of hydrogen in the gas phase at equilibrium. Using the ideal gas law, reaction (3), and assuming, as is approximately the case in the metal contained experiments discussed in this paper, that the volumes of the aqueous and gas phases are equal, it is possible to show that the Cu$^+$ activity increases approximately by a factor of 10 while the H$_2$(aq) activity and p_{H_2} each decrease approximately by a factor of 10 compared to a system with no gas volume. Exact results, including non-ideal effects, may be obtained using the PhreeqC software described above.

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