

Water Corrodes Copper

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Abstract According to a current concept, copper canisters of thickness 0.05 m will be safe for nuclear waste containment for 100,000 years. We show that more than 1 m copper thickness might be required for 100,000 years durability based on water exposures of copper for 20 h, 7 weeks, 15 years, and 333 years. An observed evolution of hydrogen *which involves heterogeneous catalysis of molecular hydrogen*, first principles simulations, thermodynamic considerations and corrosion product characterization provide further evidence that water corrodes copper resulting in the formation of a copper hydroxide. These findings cast additional doubt on copper for nuclear waste containment and other important applications.

Keywords Copper · Water · Copper hydroxide · Hydrogen · Corrosion

1 Introduction

Nuclear power plants today produce waste that needs to be stored safely for a long time and several solutions have been proposed [1, 2]. It is thought that a thickness of 0.05 m of copper buried underground will be safe for at least 100,000 years [3]. The assumption that only 0.05 m is needed relies on the ex situ characterisation of formed corrosion products [4] and a belief that corrosion of copper by water as such is impossible or negligible [3, 5, 6].

The safe storage of spent nuclear fuel must be based on knowledge of the actual reaction products, the influence of temperature, effects of hydrogen, local corrosion conditions and a margin for unanticipated environmental impact. Relevant background facts for our current study have been: (1) release of molecular hydrogen (H_2) to a gas volume will not take place in reaction of a metal with water unless the amount of molecular oxygen (O_2) is insufficient to combine with hydrogen [7], (2) in a gas-mixture of O_2 and water

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vapour a considerable part of the oxygen in the reaction product comes from water [8], (3) atomic hydrogen enters the copper metal in hydrogen evolution from corrosion in water [9], (4) only a hydrogen- and water free exposure produce a hydrogen-free corrosion product on copper [8, 10], (5) the pressure of molecular hydrogen (H_2) in ambient air is 5×10^{-7} atm and is the result of partly unknown sources and partly unknown sinks from a steady state. Therefore any process with production of $H_2 > 5 \times 10^{-7}$ atm can not be counteracted by hydrogen in our atmosphere. On the other hand the thermodynamic equilibrium of H_2 in ambient air with typical humidity, can be calculated to be a mere 10^{-43} atm [11] where this negligible pressure is due to the presence of O_2 .

The prediction made in Ref. [12] includes a metal-hydrogen bond which is absent in the reaction products assumed in the traditional thermodynamic approach. Moreover, a hydroxide rather than a hydrogen-free reaction product is expected for copper, although a printing error might have clouded the issue [12] of relevant reaction products.

Ultra high vacuum (UHV) based techniques have frequently been used in studies to find out if a certain atomic plane of a metal splits the water molecule and to identify reaction products [13]. Copper has in this approach been classified as a borderline metal. It is difficult to follow the reaction between a metal and H^+ and OH^- ions which are always present to one in approximately 10^8 water molecules in pure liquid water as a result of auto-ionisation. Given this, we have performed first principles calculations in the theoretical part of our present study to investigate the possible formation of compounds of copper and the dissociation products of water. Note, that close to the copper surface this ratio might be considerably larger [14].

Other general limitations are the poor electrical conductivity of pure water and a possible separation on a molecular level of anode and cathode (a possible redox couple exists) which make electrochemical characterisation difficult or impossible. An in situ detection of H_2 during the exposure of a metal to water is preferable to demonstrate reaction of a metal with water [13]. It should also be noted that a use of deuterium based water, although there are clear detection advantages, may not be relevant since normal water has different bonds compared to deuterium based water in combination with that copper is a borderline metal in corrosion.

2 Simulations

We performed first-principles calculations of the energy of adsorption of OH on the Cu surface. This was done with the Vienna ab initio Simulation Package (VASP) [15]

within the framework of the frozen-core all-electron Projector Augmented Wave (PAW) method [16]. The super cell with periodic boundary conditions consists of six layers of Cu atoms in the (001) direction and a vacuum layer. The OH group was positioned in vacuum at the distance of 4 Å from the surface. We used the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [17] as implemented in VASP. This functional is reliable in describing the hydrogen bonds and bulk properties of water as well as solid surface properties [14]. Fermi smearing with a width of 0.2 eV was used. The lattice constant equal to 3.635 Å compared well with the experimental value of 3.615 Å and gave a pressure very close to zero in the initial configuration. The average values of free energy (that is, the potential energy of atoms and free energy of electrons) were computed by ab initio molecular dynamics (MD) at a temperature of 300 K. We used MD runs of 5,000 time steps with duration of 0.5 fs (to account for the fast dynamics of the H atom). The temperature is maintained by the Nosé thermostat. The last 1,000 timesteps are used for computing the averages. Since the surface at 300 K is thermalized rather fast and the OH group also finds the minimum almost instantly, the number of timesteps is sufficient for retrieving reliable averages. We simulated pure a Cu surface, OH, and Cu a surface with OH.

3 Experimental Method

We have measured pressures of H_2 from copper (>99.99%) corrosion by liquid water using a palladium membrane which separates hydrogen from water, and by means of absolute pressure meters. In the present study the as-received copper was stored at room-temperature for more than a year in paper with relatively dry (30–40% relative humidity) air. The copper samples were slightly covered by a reaction product with an approximate thickness of 10 nm when used in the present exposure to pure water. This surface finish was different from the one used in [10] (polished with 1,000 mesh SiC paper) and therefore the measured phenomenon of hydrogen evolution is not dependant on the surface finish of copper, nor low levels of impurities in the copper metal.

The equipment used in the present study is made of stainless steel 316L with UHV-gaskets and is essentially the same as used previously [10]. The palladium membrane is crucial since hydrogen can quickly diffuse in this material. In the present equipment an additional absolute pressure meter above the palladium membrane further improves the detection of H_2 and direct access to a mass spectrometer, placed in UHV, verifies that a measured pressure rise is due to H_2 . The volume below the membrane was opened to an evacuated 2.3 larger volume to, as fast as possible, remove O_2 in the exposure to liquid water. This

was done 14 times in the first 10 h of the exposure and caused the total pressure to decrease to approximately 27 mbar at 21 °C which then consisted mainly of water vapour.

4 Results and Discussion

4.1 Theoretical Prediction of Corrosion

To investigate the possibility of formation of solid phases in the Cu–O–H system, we applied a thermodynamic approach as well as ab initio molecular dynamics. In the thermodynamic approach, we relied on the method of minimizing Gibbs energy of the system and, thus, determining the equilibrium composition of the system. We analyzed a number of thermodynamic databases, such as [4] and found that Cu and Cu₂O are the only stable solid phases if the fugacity of molecular hydrogen is maintained at a very low level. By introducing a hypothetical solid phase of arbitrary stoichiometry CuO_xH_y (standard thermodynamic tables do not contain data for this phase), we attempted to find out the magnitude of the standard Gibbs energy of that phase to have this phase present in the Cu–O–H system. The corresponding Gibbs energy should be lower than approximately –114 kcal/mole (otherwise this phase will not be formed). To estimate whether Gibbs energy of a possible solid phase CuOH could be lower than –114 kcal/mole, we performed the following ab initio molecular dynamics simulation.

We approximated the Cu surface by the (100) atomic planes which is illustrated in Fig. 1 and performed first principles simulations [14] of the copper–OH interaction because OH[–] is always present in water. The kinetics of water dissociation is irrelevant for the final product and affects only the rate of film formation on the copper surface. From these simulations we obtained the following energies: –363.6 eV for the slab of 108 Cu atoms, –7.6 eV for the isolated OH group, and –376.9 eV for the OH adsorbed on the Cu surface. We found that the energy of OH binding to the Cu (100) surface is -5.7 ± 0.2 eV coming from $-376.9 - (-363.6) - (-7.6) = -5.7$ eV which corresponds to approximately –131 kcal/mole since 1 eV equals approximately 23 kcal/mole. The OH group is positioned with the O atom bonded to an individual Cu atom rather than at an equidistant position (Fig. 1). The OH vector is directed somewhat outward from the surface. We also performed a similar study choosing Au instead of Cu. The Gibbs energy for precipitation of the most probable hydroxide, Au(OH)₃, according to the thermodynamic modeling is –174 kcal/mole (–7.56 eV) or lower. In the first principles simulations we obtained -3.5 ± 0.2 eV, or approximately –80 kcal/mole, which is much higher than required for Au(OH)₃ formation. That is corrosion of Au is

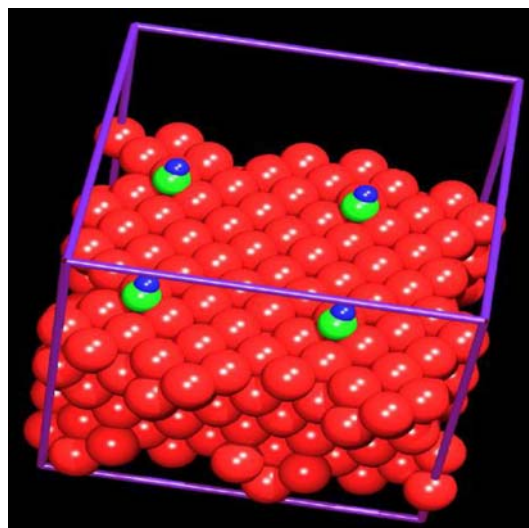


Fig. 1 The computational cell (doubled in X and Y directions) used to compute the binding energy between the OH (green and blue spheres) group and (100) surface of copper and gold respectively (red spheres). Periodic conditions are applied to the box in X, Y, and Z directions. In the case of copper the OH forms a strong bond of -5.7 ± 0.2 eV, and in the case of gold OH forms a bond of -3.49 ± 0.15 eV

forbidden or unlikely while corrosion of Cu is expected, i.e. there is a hydrogen containing corrosion product (CuOH) that is stable in pure O₂-free water. This is in agreement with the experimental observations.

Copper hydroxides converts easily to oxides, especially when exposed to air [18]. An in situ experimental technique is thus required to distinguish between possible hydroxides upon further exposure to pure water.

4.2 Measurements of H₂-Evolution

We measured H₂ from reaction of copper with liquid water at 21 °C with the results shown in Fig. 2. It is seen in Fig. 2a that H₂-evolution from copper corrosion exceeds the pressure of H₂ in air. From the simultaneous measurements of total gas pressures (below membrane) and only H₂-pressures (above the membrane) we observe a delay of hydrogen gas evolution that is mainly due to remaining molecular oxygen in the liquid. In this exposure the temperature was determined by the measured pressure below the membrane which was virtually only due to the water vapour pressure. In Fig. 2b, which is a continuation of the exposure of copper in Fig. 2a after 1600 h, is shown the influence of increasing the temperature from 21 to 45 °C, external H₂-pulses, and removal (evacuation) of gases below and above the membrane. In Fig. 2c is shown the influence of vibrations which cause an increased supply of reactants. In this figure is also shown the mitigation (inhibition) of copper corrosion.

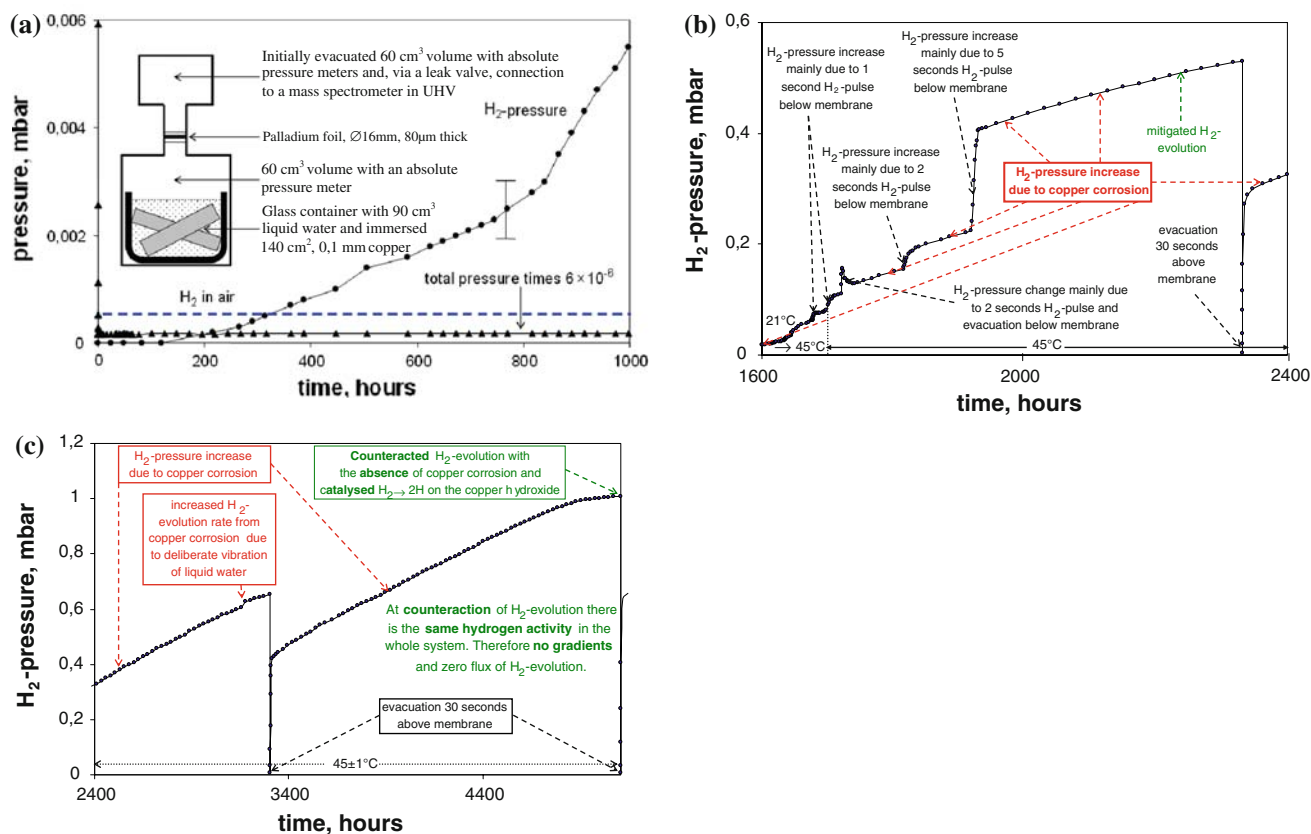


Fig. 2 a Total pressure and H_2 -pressure in exposure at 21 °C of 140 cm² copper to 90 cm³ liquid water. Gas volume above and below membrane is 60 cm³ respectively. b Continuation of exposure in a after 1600 h. Influence of increasing the temperature from 21 to

45 °C, external hydrogen pulses below membrane, evacuation below and above membrane and mitigation of H_2 -evolution. c Continuation of exposure in b. Influence of deliberate vibration, evacuation above the membrane and counteracted H_2 -release

It must also be emphasized that water always supplies the ions OH^- and H^+ via auto-ionization. Even in a perfectly closed system, the corrosion rate cannot be calculated from the detected H_2 -evolution rate since only a part of hydrogen is going to the gas phase and another part into the metal.

4.3 Experimental Prediction of a 100,000 Year Exposure

The release rate of copper from a gold-containing alloy exposed to water was followed by γ -spectrometry after irradiation of the alloy with neutrons [19]. A nm-thick surface enrichment of gold took place both on exposure of the alloy to water with 1% sodium chloride and in distilled water and was linked quantitatively to the preferential release of copper from the alloy. The kinetics of the gold enrichment was followed by X-ray Photoelectron Spectroscopy (XPS) [20] and later confirmed and detailed with high-resolution techniques [21]. From the γ -spectrometry and the XPS-data we determined the kinetics of copper removal from this alloy after only 20 h of exposure to liquid pure water. However, in this case we expect a

somewhat higher initial corrosion rate (release rate) of copper from such a copper-containing alloy than for exposed pure copper.

In 1993, an experiment comprising exposures of copper rods in distilled water at room-temperature was started. The rather dark corrosion product was analysed in 2008 [9] by Secondary ion mass spectroscopy, SIMS, a technique which can detect hydrogen in solids [22]. We could confirm that a hydrogen-containing reaction product was formed which was not due to un-dissociated water. Furthermore we could confirm that hydrogen was present in the copper metal to a considerable depth as a result of the exposure when corrosion continues due to the escape of hydrogen from the system. The maximum depth at which oxygen was observed from the reaction of copper with water was about 35 µm based on crater-depth measurements after the SIMS-analysis.

Copper coins struck in 1627–1628 were found on the warship Wasa, sunk outside of Stockholm, Sweden, in 1628 and salvaged from the mud in 1961 [23]. These coins offer probably the longest time exactly known for copper corrosion in “anoxic” water [24]. The weight, thickness, and purity (>99 wt%) of some of these coins were

determined in 1984 by one of the present authors. The salvaged coins had weight losses varying most likely due to different water access and mud coverage, explaining why many coins had a discus shape. The temperature had been approximately 5 °C over the 333 years exposure time. The appearance of two of these coins is shown in Fig. 3.

The different exposures of copper to liquid water, described in this section, are summarized in Fig. 4. In this graph we have also included our very first published corrosion data [25] in distilled water where a weight gain was reported at room-temperature (in that publication hydrogen evolution was also measured). A straight line extrapolation in Fig. 4 gives a general corrosion penetration of copper to at least 1 m when 100,000 years is considered at room-temperature, with even more corrosion penetration if higher temperatures are assumed. The slope of the straight line in this graph corresponds to an increased corrosion rate of copper with time and is most likely due to the uptake of hydrogen in copper with a poorly protective and non-adhering reaction product. This negative influence of hydrogen on corrosion kinetics has also been reported for iron, iron based alloys [26, 27] and on copper doped with deuterium [28].

4.4 Some General Considerations

Copper exposed to water in the absence of dissolved O₂ is subjected to mild corrosion under hydrogen evolution. The corrosion process can continue in all systems where dissolved hydrogen is allowed to be transported away. The

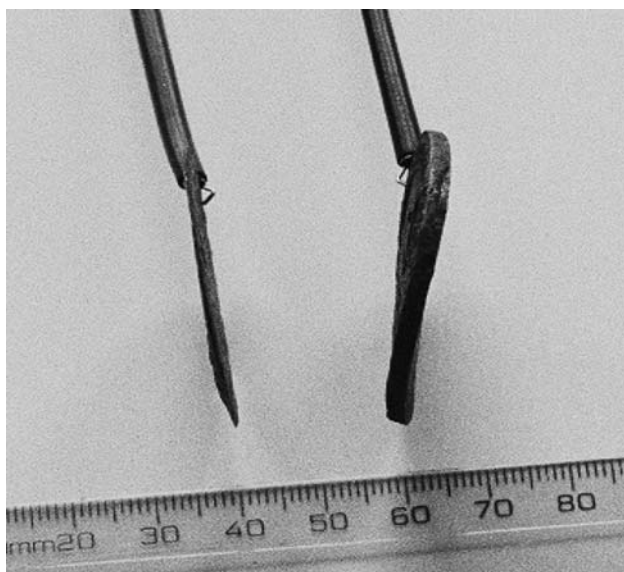


Fig. 3 The thin “1 öre” copper coin to the left had lost weight and the thick coin to the right had gained weight due to varying access of water with negligible molecular oxygen during the 333 years exposure

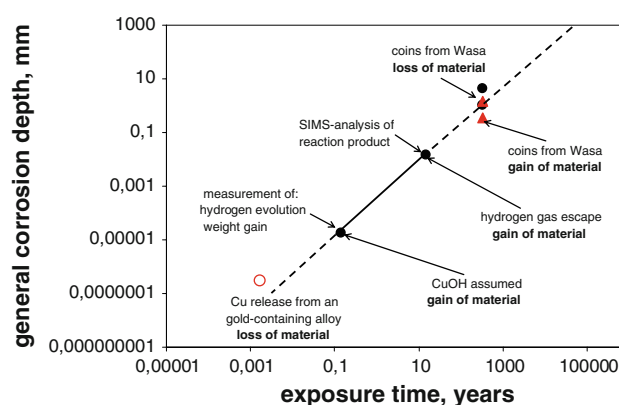


Fig. 4 The shortest time in this graph is from measurements of the release rate of copper from a gold-containing alloy exposed to water. Data from the approximately 7 weeks exposure are taken from Ref. [24]. Data from the 15 years exposure are taken from the corroded rod in Ref. [9] with SIMS- and crater depth analysis. A 3.5 times higher value for the circles (room-temperature) than for the triangles is used where the latter are the influence of 333 years corrosion at 5 °C of coins found on the warship Wasa. (Examples shown in Fig. 3). The straight line is hatched down to the shortest exposure time of 20 h and for longer times than 15 years and solid when distilled water is used with detection of hydrogen. Error is estimated to be the size of the respective data point. The straight line extrapolation in the current figure gives a corrosion penetration of at least 1 m if 100,000 years at 20 °C is considered

evacuations in Fig. 2 are analogous with the escape of hydrogen in real life where it can take place via diffusion and ultimately combine with oxygen outside the copper-water system. (This is shown in Fig. 5 in [10]). Copper oxides are thermodynamically possible underneath a hydroxide layer, provided that the hydrogen activity is not high enough to reduce the oxide. The kinetics of both the reaction $2H \rightarrow H_2$ and the reduction of the copper containing reaction product by means of H₂, are catalytically ruled and are therefore material and surface dependant. This is analogous with the catalytic properties among different materials in O₂-exposure [11].

We find that the ultimate reaction product on exposure of copper to water is a copper hydroxide which is not well-characterized using X-ray diffraction. We have reported that the hydrogen pressure required to counteract copper corrosion in liquid water is at least 1 mbar at 73 °C [16] and here we find mitigation of H₂-evolution at approximately 0.5 mbar at 45 °C and counteraction at approximately 1 mbar. These pressures can not be calculated simply by assuming the stability of an ex situ characterized product like Cu₂O as has been done in Ref. [6]. The inhibition of copper corrosion is measured via a hydrogen pressure above the liquid water. The counteraction of copper corrosion is determined by several factors, like the solubility of hydrogen in water and in copper as well as catalytic activities, which means that any activation energy for the overall process is difficult to fully interpret.

5 Conclusions

- There is an evolution of hydrogen in reaction with copper metal in liquid water at room-temperature which is evidence for corrosion of copper by water. This hydrogen evolution takes place up to a pressure which greatly exceeds the hydrogen pressure in air.
- Early experimental results, favoured hydroxide formation, and our first principles simulations concerning copper stability are consistent with our present experimental results which involves catalytic properties of a copper hydroxide.
- Contrary to the accepted view, pure water does indeed corrode copper.
- By linking together exposures with widely varying durations of copper to liquid water without or negligible O₂, a realistic extrapolation is made to predict that more than 1 m thickness of copper is required for a 100,000 year lifetime at room-temperature.

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