

DEPARTMENT OF MATERIALS CHEMISTRY  
UPPSALA UNIVERSITY

# Copper corrosion in pure oxygen-free water

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Research project

1 October 2010



## RESEARCH PROGRAM

The proposed project is a fundamental research study of copper corrosion processes in water free from dissolved molecular oxygen, in this report named oxygen free water or pure water.

### Specific aims

- To carry out experimental studies that allow quantification of hydrogen as a product of the reaction between copper and water.
- To monitor and exclude, if possible, other reaction products which may form.
- To recover and characterize reaction products between copper and ultra-pure water.

### 1. Introduction

Copper was chosen about 30 years ago as a container material for nuclear waste disposal in Sweden. The canisters for nuclear waste disposition are planned to be made of pure copper with walls about 5 cm thick, to be embedded in bentonite and buried in the rock. Those containers are designed to be safe for nuclear waste containment for at least 100 000 years. The primary reason for choosing copper is that it should be thermodynamically stable under the anaerobic conditions expected in the long term in granitic repositories.

The chemical stability of copper in contact with granitic rock has been widely studied by several research groups [1-5], and it was concluded that dissolved sulphide, oxygen and chloride in groundwater are the most damaging components for copper. In the absence of those components dissolved in water copper is considered to be immune to corrosion damage [6-7].

However, corrosion of copper by oxygen-free water has been reported by P. Szakálos *et al.* [8]. These authors claim that the corrosion of Cu, accompanied by hydrogen gas evolution, occurs spontaneously in pure de-ionized, oxygen-free water at 73°C. These observations are in line with other experimental studies made by Hultquist *et al.* [9-11], where the corrosion of copper by pure water was postulated. Moreover, G. Hultquist and P. Szakálos *et al.* made a prediction based on experimental data and theoretical calculations, that more than 1 meter of copper is required for a 100 000 years lifetime of copper canisters [12].

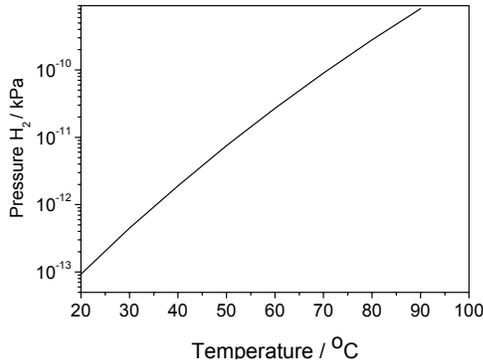
Attempts to reproduce the results presented by G. Hultquist and P. Szakálos have been made by other research groups [13-14]. No hydrogen evolution by corrosion of pure copper in water has been registered experimentally. The findings presented in refs. [8] and [12] have been criticized [15,16] as inconsistent with *basic* thermodynamic data on the copper oxygen system [3,17-19], for example with a *classical* Pourbaix diagram for Cu-H<sub>2</sub>O system [17,19]. However, in a recent

study [20] the thermodynamic stability was calculated of the species adsorbed on a copper surface ( $\text{H}_2\text{O}_{\text{ads}}$ ,  $\text{OH}_{\text{ads}}$  and  $\text{H}_{\text{ads}}$ ) in water. They also showed a possible Pourbaix diagram where the adsorbed OH monolayer is more stable than bulk  $\text{Cu}_2\text{O}$  [20].

### 1.1 How can copper be corroded by water?

Under normal conditions in water, copper is oxidized by oxygen gas dissolved in the water. Under anoxic conditions in neutral water, copper oxidation is not energetically favorable and is not expected to occur at any significant rate, following reaction routes normally cited in the literature [3].

Fig. 1 shows the equilibrium partial pressure of hydrogen as a function of the system temperature as calculated by a minimization of Gibbs free energy for the system  $\text{Cu}/\text{H}_2\text{O}$  [21]. As can be seen, the equilibrium partial pressure of hydrogen for copper in pure water is only  $2 \cdot 10^{-13}$  kPa at 25 °C and 1 atm total pressure but increases logarithmically to  $8 \cdot 10^{-10}$  kPa at 90 °C, which still is a lower value than the naturally occurring partial pressure of hydrogen in air ( $5 \cdot 10^{-8}$  kPa). One should remember that the result in Figure 1 was calculated for a closed system, i. e. at equilibrium.



**Fig. 1.** Partial pressure of hydrogen in equilibrium with copper and pure water calculated by minimization of the Gibbs free energy of the system  $\text{Cu}/\text{H}_2\text{O}$ .

The underlying chemistry has been elucidated in details by Shoesmith in the seminars held at SKB in November 2009 [22]. Still, Hultquist and co-workers have detected hydrogen in significant amount in experiments published during the past 20 years.

Thus, in his experimental study [9], G. Hultquist assumed that copper corroded to  $\text{Cu}_2\text{O}$  according to:



The evolution rate of hydrogen at 25°C was  $15 \cdot 10^{-6} \text{ g} \cdot \text{h}^{-1} \cdot \text{m}^{-2}$ , equivalent to a corrosion rate of 0.98  $\mu\text{m}/\text{year}$ .

In the later studies Szakálos *et al.* [8] refined their argumentation and suggested that the oxidation of copper occurs with the formation of an intermediate product based on the following reaction:



The partial pressure of hydrogen gas was found to be  $10^{-3}$  bar when  $\text{H}_x\text{CuO}_y$  and Cu are in equilibrium [8]. To explain the hydrogen evolution observed in experiments [8,12], the authors postulated the existence of a previously unknown phase, copper oxy-hydride  $\text{CuH}_x\text{O}_y$  ( $x \approx y \leq 1$ ), which is stable enough to decompose water. X-ray diffraction of the corrosion products formed on copper did not reveal any new phase, so the authors concluded that the phase could be structurally described as "protonated" cupric or cuprous oxide,  $\text{CuH}_x\text{O}_y$  [8] or in later studies [12] as CuOH, i.e.  $x=y=1$ . Indeed, the existence of OH monolayer adsorbed on Cu(111) surface has been shown in Ref. [20]. CuOH has also been reported as an intermediate product of the copper corrosion process [23,24].

Thermodynamic calculations of the stability of copper compounds [25] show that oxy-hydrides,  $\text{H}_x\text{CuO}_y$ , are unstable even with respect to decomposition into cuprous oxide and hydride, while CuOH may exist but is only metastable and should decompose into  $\text{Cu}_2\text{O}$  and  $\text{H}_2\text{O}$ . The presence of oxy-hydrides remains to be confirmed experimentally.

## 1.2 Calculation of the copper corrosion rate from the measured hydrogen evolution

The copper corrosion rate under anoxic repository conditions can be calculated from the hydrogen evolution data presented in refs. [8,9,12]

In [12] Hultquist *et al.* reported the hydrogen pressure increase as 0.7 kPa/2000 hours. If we assume that 1 hydrogen molecule corresponds to 1 Cu atom oxidized to  $\text{Cu}^{2+}$ , the Cu corrosion rate in this case equals to 3.7 nm/year or  $0.037 \text{ cm}/100000 \text{ years}$ .

In the other experimental study by Szakálos *et al.* [8], they measured a hydrogen release rate of  $0.37 \text{ ng} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$ , which was calculated from the ion pump current increase. This value corresponds to a Cu corrosion rate of about  $10^{-5} \text{ cm}/\text{year}$  or  $1 \text{ cm}/100000 \text{ years}$ .

In earlier studies made by Hultquist [9], a value of 0.98  $\mu\text{m}/\text{year}$  or  $9.8 \text{ cm}/100000 \text{ years}$  was reported.

The large discrepancy in the hydrogen evolution rates measured by the same research group indicates that probably not all factors that may influence the hydrogen detection sensitivity were completely controlled in the experiments described by Hultquist, Szakálos *et al.*

One should take into consideration that the evolved hydrogen can be partially dissolved in water and in metallic Cu reducing the amount of hydrogen released to the gas phase. However, as it is known in literature the equilibrium solubility of hydrogen in Cu at atmospheric pressure and room temperature is negligibly small (less than  $10^{-6}$  H/Cu) [26-28].

### 1.3 Hydrogen detection methods

The corrosion rate of copper in oxygen-free water can be estimated by measuring the hydrogen evolution rate while copper is immersed in pure water. The hydrogen evolution rate can be measured by the following methods:

#### 1) **Gas-chromatography.**

Gas-chromatography is used to separate and analyze compounds that can be vaporized without decomposition. The gas-chromatograph can measure the hydrogen gas concentration as low as 1 ppmv. Several attempts to detect the hydrogen evolution from copper in pure water by using gas-chromatography have been made [13,14]. However, no hydrogen was detected even at evolution rates lower than those reported by Hultquist [9].

#### 2) **Hydrogen sensors.**

Many kinds hydrogen sensors which can operate in wide temperature and concentration ranges have been reported [29]. Thus, Pd- based sensor devices can measure the hydrogen concentration from a few ppm to 100% due to the changes in their capacity/resistivity during the hydrogen uptake [30,31].

#### 3) **Ultrahigh vacuum experimental arrangements.**

The method is based on the registration of the total (hydrogen) pressure increase in an UHV system connected through a palladium membrane to the vessel containing the Cu foil immersed into the pure oxygen-free water. One detailed set-up description is given in ref. [8]. Two experiments were described:

1. The *ion pump experiment* where the increase of the ion pump current was attributed to the hydrogen production rate.
2. The second experiment was the *pressure gauge experiment* that allows the direct measurement of hydrogen pressure during exposure of copper to de-ionized water.

#### **1.4 Factors which affect the detection of hydrogen in a UHV experimental set-up**

Factors that may influence the detection limit of H<sub>2</sub> in a UHV system, are the following:

1. Leaks in the UHV system.

Even in a perfectly closed system interior leaks such as micro pores and cracks may be present.

2. Out-gassing process from austenitic stainless steel vessels and UHV glue.

The out-gassing rates from the steel chamber can be strongly decreased by a vacuum bake-out at 150°C during a couple of days [32]. Before using the vacuum sealant in the UHV chamber, one should consider that it can be used only at a temperature up to 120°C and pressure below 10<sup>-9</sup> mbar.

3. Palladium membrane properties.

Palladium membranes can be used for separation and purification of hydrogen. Palladium has several advantages over other membrane materials because of its catalytic surface, high selective hydrogen permeability, and good corrosion resistance. The hydrogen permeability of a palladium membrane depends on the temperature and pressure [33]. Stress and defects of the membrane due to hydrogen cycling also influence the permeability of palladium [34].

All these factors cannot be excluded in a single experimental study. However, they can be controlled by tailored experimental arrangements, as described below.

## 2. Project description

The corrosion process is probably very complex and the products are located both at the interface and in the water solution. Since the corrosion process is slow, a thin layer of copper (I) or copper (II) oxide, hydroxide, oxy-hydride [8] may form on the Cu surface. One should consider that possible corrosion products like hydroxides or hydrides may be unstable when exposed to air, heat or irradiation, i.e., care must be taken when transferring the copper foil for surface analysis.

It is planned to maintain the set-up for the hydrogen registration, to carry out experimental studies and to provide a careful investigation of all components involved in the reaction between pure metallic copper and oxygen-free water. In particular, it is planned to analyze chemical and physical properties of copper foils (in bulk and on surface), pH of the solution and the hydrogen gas evolution rate.

### 2.1 Sample preparation

Mechanically and electrochemically polished oxygen-free copper foils made of pure Cu (99.99(9)% purity, 0.5 mm thick), will be heat-treated in inert atmosphere to release water, oxygen and hydrogen from the surface. Notably, the quality of the copper surface is important for the further investigation of the corrosion products.

### 2.2 Experimental design for gas evaluation studies

The experimental arrangement is based on the UHV set-up used by Hultquist *et al.* [8] and is shown in Fig. 2. It will be leak-checked, baked-out and placed into a glove-box filled with pure nitrogen having typically less than 1 ppm of oxygen. The glove-box is important since the experiments outside the UHV set-up such as loading and unloading can be made in a controlled atmosphere. The glove-box will also reduce the influence by small leaks on the UHV set-up that either were not detected during the leak tests or leaks that may develop with time. The sample preparation and opening of water containers will therefore be made in the glove-box.

*Three main setups* (Fig.2) are planned to run in parallel for 12 months. Three separate glass beakers will be placed into 3 stainless steel vessels separated by a palladium membrane from the UHV chamber with continuous pressure monitoring. The vessels will contain:

1. One beaker with only high purity oxygen-free water. This is to monitor zero-level hydrogen release, if any.
2. One beaker with Cu foil immersed in high purity oxygen-free water;

3. One Cu foil immersed in perchloric acid, diluted so as to produce a low, but continuous flow of hydrogen (if present) to provide an upper limit for the experiment.

The set-ups №1 and №3 are proposed as reference experimental arrangements. Ideally, set-up №1 should not show any hydrogen evolution above the background level of hydrogen. Note that the presence of hydrogen gas cannot be avoided in UHV system. Set-up №3 is expected to produce the necessary amount of hydrogen that can be detected.

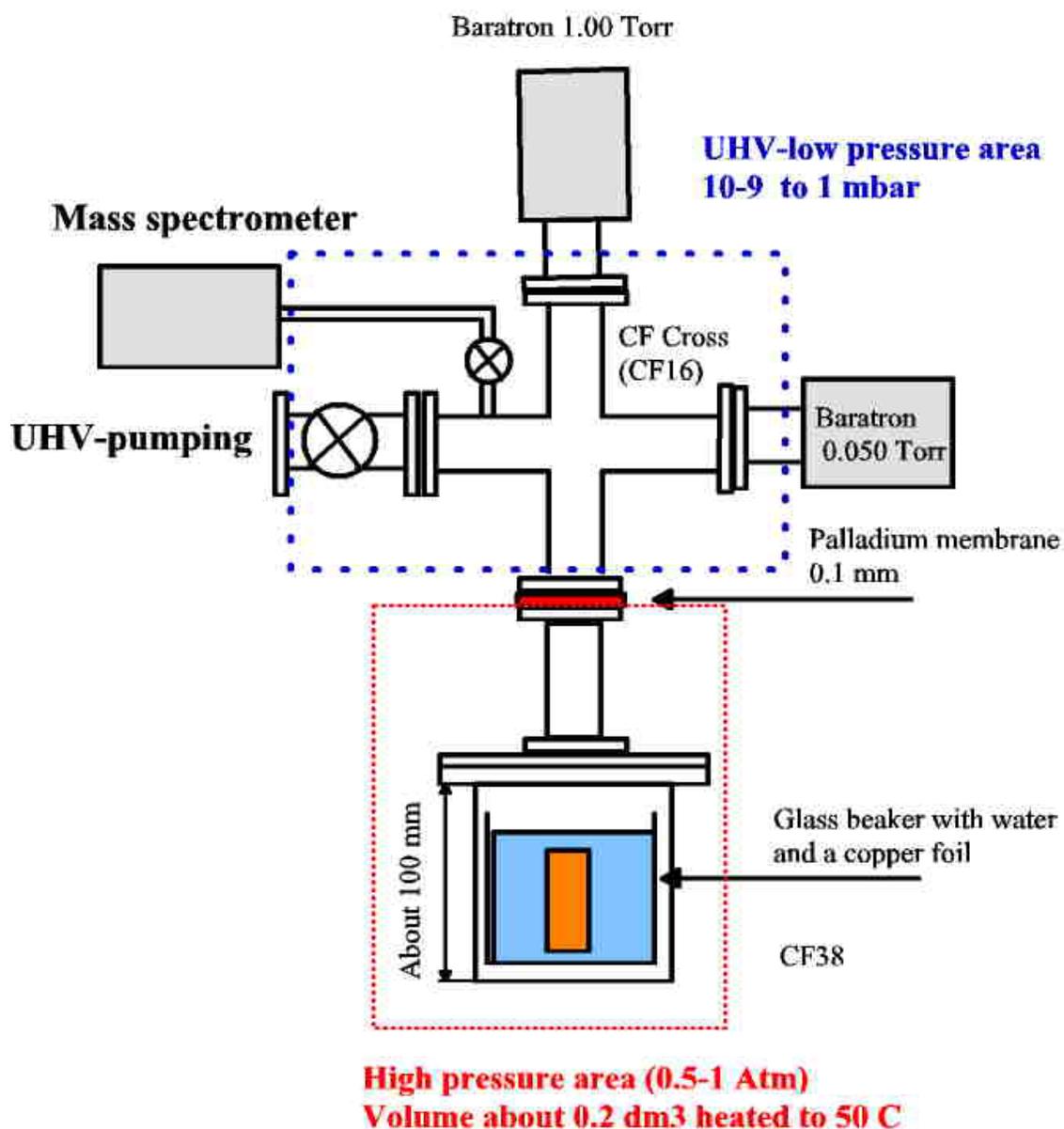
### **2.3 Experimental design for copper corrosion studies**

*Parallel experimental studies* will be carried out for intermediate checking of the Cu corrosion products at different periods of time. Ten beakers sealed with palladium membrane but without pressure monitoring (see Fig. 3) will be exposed to nitrogen atmosphere in a glove-box:

1. Five beakers with copper in high purity water (milli-Q water)
2. Five beakers with copper in perchloric acid

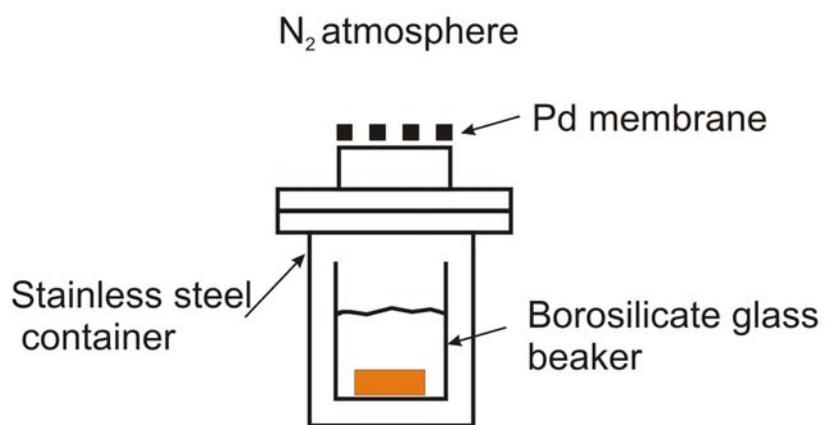
The first beaker will be opened after 1 month from the experimental procedure start, the second after 2 months, and the others after 3, 5 and 8 months, respectively. Each time analyses of the copper surface layer and the water will be performed.

## Vacuum system for measurements of hydrogen production during copper corrosion.



**Fig. 2.** Schematic drawing of the experimental set-up for registration of the hydrogen evolution when Cu is immersed in water.

## Parallel experimental arrangements



Cu in oxygen-free H<sub>2</sub>O and diluted HClO<sub>4</sub>

**Fig.3.** Schematic picture of the parallel experimental set-up without pressure monitoring.

## 2.4 Experimental conditions

The following experimental conditions are suggested:

1. Palladium membrane of a standard quality (99.99% purity, Goodfellow Inc.) between the chambers will be pressed by the copper gaskets. The gas that evolves through the palladium membrane will be monitored monthly with a mass-spectrometer.
2. All parts of the equipment will be cleaned and baked-out
3. Test temperature 50°C.
4. Ultra high purity water (Milli-Q). The containers with this water will be only opened under inert gas atmosphere in the glove-box.
5. The water will be administered to the beakers under inert conditions.

## 2.5 Experimental equipment

Below is a list of the experimental equipment, which will be used in the experimental procedure:

1. Glove-box with humid nitrogen atmosphere that has room for 3 + 10 vessels. The glove box will contain all containers under protective atmosphere for the entire duration of the experiment. All samples are transported in special containers under high vacuum or in a protective atmosphere to the analytical facilities.
2. 3 vessels for monitoring of the hydrogen evolution according to the drawing in Fig. 2.
3. 10 vessels for intermediate term detection of corrosion products according to the drawing in Fig.3.
4. 13 glass beakers in borosilicate glass for placing samples with a volume about 5 dl.
5. “Intelligent solution” for placing the samples in electrolyte, and to ensure that all metal surfaces have equal contact to water.
6. One mass spectrometer for detection of hydrogen.
7. 3 absolute pressure gauges ( $p < 1$  Torr)
8. 3 absolute pressure gauges ( $p < 0.05$  Torr)
9. Min (3 + 10) plus extra safety palladium membranes for sealing the vessels
10. Heating control, thermocouples for feedback. Interface: RS232 or equivalent.

11. Heating bands, for temperature control and system bake-out
12. Data logging system

The set-up must be tested before the experimental procedure will be carried out.

## **2.6 Evaluation of the results**

The investigation of corrosion products will be made after each take-out of intermediate samples and after the experiment is finished. The following parameters will be evaluated.

### ***Gas phase:***

1. Hydrogen pressure increase will be continuously monitored. Gas phase verification will be provided using a mass spectrometer;

### ***Sample:***

2. Weight loss of copper foils;
3. Optical properties of a copper surface will be studied by using light optical microscopy (before and after the experimental procedure);
4. The corrosion rate will be estimated by cathodic reduction of oxide on the samples. Mass balance with weight loss and solution analysis will be provided;
5. Surface roughness will be checked before and after the experiment;
6. Identification/documentation of corrosion products by combined phase analysis and analysis of the liquid;
7. The study of the chemical compounds on the copper surface will be made before and after the experimental run;

### ***Liquid phase:***

8. Analysis of reaction products in water;
9. *pH* of the solution will be checked after the experimental run. Measurement before would contaminate the solution.

## **2.7 Experimental methods to study copper corrosion products**

To study the reaction products between copper and water the following methods can be envisaged:

1. The thickness of the surface layer as well as its composition can be studied by XPS analysis. XPS will give information about the oxidation state of copper. If the thickness of

the reaction products is thicker than several nm, XPS can also give this information as a function of depth. If a very high spatial resolution is needed, Auger Electron spectroscopy (AES) can be used, otherwise XPS is preferred. ToF-SIMS is another method that can be considered.

2. Inductively coupled plasma mass spectrometry (ICP-MS) may be used to measure trace amounts of elements in the water. The detection limit for Cu in solution is  $2 \times 10^{-11}$  g/mL.
3. GD-OES (Glow discharge optical emission spectrometry) for hydrogen concentration gradients in Cu.
4. FTIR (Fourier Transform Infrared Spectroscopy) and Surface Enhanced Raman spectroscopy may be used to monitor O-H, Cu(I)-O, Cu(II)-O etc. vibrations. It is one of the methods that can, in principle, be used *in situ*.
5. X-ray diffraction and grazing incidence X-ray reflectivity studies may be exploited to estimate the thickness and composition of superficial films if they are thick enough to be studied (it depends on surface roughness).
6. Cu cathode reduction method allows for estimating the total amount of oxidized copper.
7. pH of the water solution may be monitored after immersing the Cu foil into the water.
8. Further, one can use Soft X-ray spectroscopic analyses (XAS and XES) to distinguish between Cu(I) and Cu(II) in the valence band as well as between oxides and hydroxides.
9. Ellipsometry technique with tunable wavelength can be used to determine the oxide nature and thickness.
10. Atomic Force Microscopy (AFM) is a powerful technique to determine surface morphology.

Most of the techniques are available in the Ångström Laboratory, Uppsala University. XAS and XES are accessible in MAX-lab National Laboratory for Synchrotron Radiation in Lund. ToF-SIMS and AES spectrometry are accessible at the Dalarna University, Borlänge. International facilities, such as beam lines at ESRF and BESSY can be used for spectroscopy and diffractometry.

## 2.8 Time schedule and results

The proposed study is scheduled for:

- Equipment ordering, purchasing and maintenance –from 3 to 6 months (the upper limit is given for longer purchasing time);
- Experimental run- 1 year;
- The analysis of corrosion products after 1 year experiment and report writing: 6 months.

Totally 24 months.

The study will result in a written report in English with an extended popular summary in Swedish and eventually, one or two manuscripts will be submitted to a scientific journal.

The findings of this study aim to unravel the mechanism of copper interaction with oxygen-free water and either confirm or eliminate oxygen-free water as an essential factor for corrosion of the copper canisters for the nuclear waste disposal.

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