

# **DRAFT REPORT 2009-11-04**

## **Comments regarding the BRITE report, SSM 2009-30, “A Review of Evidence for Corrosion of Copper by Water”**

Ph. D. Peter Szakálos, Royal Institute of Technology, Stockholm, Sweden

The Swedish Radiation Safety Authority (SSM) has a reference group named BRITE (Barrier Review, Integration, Tracking and Evaluation) who has made a review of corrosion of copper by water. This was done on request by the Swedish Nuclear Power Inspectorate, SKI (now renamed SSM).

Peter Szakálos and Gunnar Hultquist, were invited by SKI to attend a meeting with the BRITE-group, 2008-05-12, when we gave a presentation and answered questions related to our research on copper corrosion by water. The BRITE-group wrote after that the report “A Review of Evidence for Corrosion of Copper by Water”<sup>1</sup>. The review report concerns only one of our publications<sup>2</sup>. SSM have now asked us to comment the BRITE report and to answer some specific questions related to copper corrosion by water.

### **PART 1. LITERATURE REVIEW**

#### **Native copper metal in the Swedish groundwater?**

Copper is not considered as a noble metal<sup>3</sup>. However, in the KBS-3 model it has been assumed that copper is thermodynamically immune in pure water<sup>4</sup>

One argument for this assumption of immunity is the existence of native copper in the earth's crust. However, also metals such as Fe, Cr, Ti and Zn are found in the metallic state at some locations<sup>5</sup>. This is also the situation for copper; only some per thousand of copper in the earth's crust exists in the metallic state and then concentrated to only a few locations<sup>6</sup>.

This argument only implicates that the hydrogen activity was sufficiently high and the sulphur activity was sufficiently low for metallic copper to be deposited in a specific location during a certain event in the geological history. The water and oxygen activities and different ion activities must then have been sufficiently low in such a location to preserve at least a core of native copper and of the other metals. In almost all positions in the earth crust, it is expected that copper is not immune. On the other hand, noble metals such as gold and platinum exist to at least 99% as native metals in the earth's crust.

Thermodynamic experts confirm that the presence of native copper in some few locations on the earth is not an evidence for copper immunity in any other location such as in the Swedish groundwater. On the contrary, since only copper minerals such as sulphides are found in Sweden it is a strong indication that copper is not thermodynamically immune in the Swedish groundwater<sup>7,8,9</sup>. Thus, no copper immunity region is expected in the Pourbaix diagram for the anticipated repository environment, see Figure 1.

## Thermodynamic considerations – Anoxic environments

There have been some questions from the BRITE-group regarding the term anoxic. We have used the following definition of the term: In practice “anoxic water” includes all water environments with more dissolved hydrogen (H<sub>2</sub>) than dissolved oxygen (O<sub>2</sub>). Theoretically, the borderline situation with equal amount of dissolved H<sub>2</sub> and O<sub>2</sub> in equilibrium with water is represented by a line in the Pourbaix diagram.

According to Nernst equation, this corresponds to a gas phase with a total pressure of 10<sup>-28</sup> bar, see Figure 1. This could colloquially be regarded as water without dissolved gases. Anoxic water gives a rather low redox potential compared to water in contact with air. However, below this redox potential line in the Pourbaix diagram both monovalent and divalent corrosion products are thermodynamically expected to form on copper.

## The surface reaction route in corrosion

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 (from a O<sub>2</sub>-free gas phase) and to identify reaction products<sup>10</sup>. Copper has in this approach been classified as a borderline metal. In previous isotope studies with gas mixtures of <sup>16</sup>O<sub>2</sub> and H<sub>2</sub><sup>18</sup>O it was demonstrated by Hultquist that most of the oxygen in the corrosion product on iron<sup>11</sup>, chromium<sup>12</sup> and copper<sup>13</sup> surfaces originates from reaction with the water and not with the oxygen.

For these metals a considerable part of the consumption of the O<sub>2</sub> takes place via the hydrogen-oxygen reaction (2H<sub>ads</sub> + O<sub>ads</sub> → H<sub>2</sub>O) where adsorbed H is produced from the reaction of metal with water. The surface catalysed hydrogen-oxygen reaction on iron and copper<sup>13</sup> is faster than the formation rate of the initially produced atomic hydrogen from the corrosion reaction itself. This means that it is not possible to detect any hydrogen release from copper and iron as long as the supply rate of O<sub>2</sub> to the surface exceeds the rate of hydrogen generation.

It is difficult to follow the reaction in pure liquid water between a metal and H<sup>+</sup> and OH<sup>-</sup> ions which are always present to one in approximately 10<sup>8</sup> water molecules as a result of auto-ionisation as discussed in<sup>2,14,15</sup>. Other limitations are the poor electrical conductivity of pure water and a possible separation on a molecular level of anode and cathode on the metal surface which make electrochemical characterisation difficult or impossible<sup>15</sup>. An *in-situ* detection of H<sub>2</sub> during the exposure of a metal to water is preferable to demonstrate the reaction of a metal with water<sup>10</sup>.

## Copper corrosion by water

It has been shown both experimentally and theoretically that copper do split the water molecules from water vapor, i.e. a gas phase without O<sub>2</sub>. “With Ab-initio calculations it has been shown that Cu (110) is the borderline between intact and dissociative water adsorption, differing in energy by only 0.08eV. This may lead to promising applications in hydrogen generation and fuel cells.”<sup>16</sup>. Experimentally it has been shown in 1 torr water vapor at ambient temperature that Cu (100) surfaces indeed dissociate water molecules<sup>17</sup>.

In our latest publication we have shown that copper reacts with water molecules and that CuOH is thermodynamically favored at room temperature<sup>15</sup>. “By introducing a hypothetical solid phase of arbitrary stoichiometry CuO<sub>x</sub>H<sub>y</sub>, 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.”

By analyzing eight thermodynamic databases it could be concluded that the 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 *ab initio* molecular dynamics simulations at 300K. The results showed that the standard Gibbs energy of CuOH is approximately -131 kcal/mole. This is a low value, indicating that CuOH is a really thermodynamically stable product. Thus corrosion of Cu is expected, i.e. there is a hydrogen containing corrosion product (CuOH) that is stable in pure O<sub>2</sub>-free water. This is in agreement with our experimental observations. It is difficult and time consuming to find out theoretically, whether an amorphous bulk phase CuOH is expected. To our knowledge this is never done.

It may be pointed out that an amorphous copper hydroxide converts easily to oxide, especially when exposed to air<sup>18</sup>. Therefore, an *in-situ* experimental technique is thus required to distinguish between possible hydroxides at exposure to pure water.

### **The known thermodynamics about copper corrosion is incomplete**

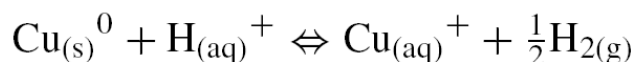
There are surprisingly many published studies about copper corrosion in water environments that concludes that there is something missing in the thermodynamic description of copper corrosion. Here follows some examples from the peer reviewed literature.

#### ***Review of literature regarding copper corrosion studies in anoxic water environments:***

Copper corrosion by pure water in copper cooling systems is widely observed and a severe industrial problem internationally e.g. of copper stator cooling systems in generators for electric power production. Irrespective of how the water is treated, deionised and degassed etc, the copper channels in the stator windings are clogged with copper oxides and hydroxides after some years in service. Similar problems are observed in cooling systems for particle accelerators and in research fusion reactors. It is common to add a separate filtering device i.e. strainer in industrial cooling systems to take away the corrosion products from the cooling water.

A general observation is that irrespective of what water chemistry concept used, copper does corrode in pure and deaerated water with a corrosion rate at 40°-70°C in the range of 0.5-10 µm/year<sup>19,20</sup>.

Researchers working with the ITER-project have concluded that anoxic copper dissolution does occur in pure water under hydrogen formation according to the reaction:



However, the copper solubility are more than “four or five orders of magnitude larger than the copper solubility obtained by thermodynamic data”. The measured concentration in this

particular experiment at 100°C was 33 µg/kg “in a steady state condition” as shown in Fig. 4. One possible explanation for this remarkable deviation from known thermodynamics is the presence of “another Cu-species”<sup>21</sup>.

The performance of low-conductivity water cooling systems is of critical importance at particle accelerator facilities as well as in stator cooling systems for electric power generators. A summary from the experience from these copper cooling systems is that “The copper corrosion can be minimized but not prevented”<sup>20</sup>

Russian researchers have studied copper corrosion in pure water containing dissolved hydrogen gas, i.e. at low redoxpotentials and they concluded that copper corrosion slows down, by the addition of hydrogen, but can not be prevented completely under the experimental conditions used<sup>22</sup>.

Copper pipe corrosion have been studied in potable water with oxygen scavengers according to the standardised method 4500-O G which “ensure complete removal of dissolved oxygen”. “These results indicate that something besides (or in addition to), the reduction of oxygen” is driving the corrosion<sup>23</sup>.

A recent study of copper corrosion in synthetic drinking water during stagnant conditions, reveals that “the available concentration of hydrogen ions, rather than dissolved oxygen, is the limiting factor for copper release into drinking water” “Furthermore, copper release into water is not limited by the amount of dissolved oxygen. Rather, the results indicate that the mass of hydrogen ions that controls and limits the solubility of the solid corrosion by-products, along with the oxidation of the metallic copper.”<sup>24</sup>

Hot copper surfaces in contact with pure water have a surprisingly high solubility<sup>21</sup> and it is believed that copper corrodes by a dissolution-precipitation process. This means that copper corrosion products may precipitate not only on copper surfaces but on any surface. This is, for instance, observed in stator cooling systems where copper corrosion products are precipitated and growing on strainer plates as shown by a SEM-study in a patent application<sup>41</sup>, see Figs 2a-d and 3a-b.

Regarding the copper dissolution-precipitation process it is stated that “This fact has implications on the KBS-3 model, since hot copper is in contact with the bentonite pore water and in the pH range of interest, pH 7-9, the negatively charged faces of bentonite particles, as well as the edges which are negatively charged in this pH range, represent a large surface for precipitation of copper corrosion products, thus driving the anoxic copper corrosion further.”<sup>42</sup>

This corrosion process has been observed and the corrosion rate is found to be in the order of 1000-10000 times higher than anticipated by the KBS-3 model<sup>25,26</sup>. A copper tube was placed in wet bentonite and heated for 5 years within the LOT-project in the Äspö laboratory. It was shown that the copper corrosion was several µm/year<sup>26</sup> and with the knowledge that the dissolved oxygen is consumed within the first days or first weeks of exposure<sup>27-29</sup> it must therefore be concluded that most of the corrosion has taken place under strictly anoxic condition. In Ref. 25, page 1991, it was concluded that “O<sub>2</sub>-transport was not rate-limiting” and that the corrosion took place with a dissolution–precipitation process; “Precipitation of copper inevitably occurred in all of the tests, with usually more than half of the total copper corroded being in the form of precipitate rather than being sorbed on the clay”. In the 5-year

LOT-project it was confirmed that a significant part of the corrosion products was precipitated up to several centimetres from the copper surface in the bentonite clay. Furthermore, it was shown that at least some part of the corrosion products had precipitated as copper sulphides and copper-iron sulphides, thus confirming a low redoxpotential and anoxic environment.

In Ref. 27, SKB report TR-01-05 entitled “O<sub>2</sub>-depletion in granitic media”, the REX project, it is stated in the abstract regarding the field investigations in Äspö:

“The results from the in-situ experiments were confirmed by those of the replica experiment performed in the CEA laboratory in France. Both were concordant in showing time scale for O<sub>2</sub> uptake in the order of days.”

In Ref. 28 it is stated that: “Laboratory experiments with bentonite suspensions, 18 to 73 g/L, showed that: - In all experiments O<sub>2</sub> was depleted within a few days”

### ***Additional corrosion studies in alkaline water and groundwater environments:***

Most metals forms a hydroxide in contact with water and under the hydroxide an oxide is normally formed and it seems that copper metal is not an exception in this case as discussed here below.

Anodic dissolution of copper in alkaline solution has been studied by Pyun et al.<sup>18</sup> It was shown that Cu(OH) is in equilibrium with Cu<sub>2</sub>O at lower redoxpotentials and that Cu(OH) easily converts to its “aged product” Cu<sub>2</sub>O. Furthermore, it was concluded that the initial anodic oxidation may be summarized as:  $\text{Cu} + \text{H}_2\text{O} = \text{Cu}(\text{OH}) + \text{H}^+ + \text{e}^-$ .

Kuntze et al.<sup>30</sup> have also studied the initial stages of copper corrosion. A partially ordered surface hydroxylation (CuOH) was observed at very low redox potentials, -810 mV (SHE) at pH 13. This hydroxylation exists also at higher potentials on the surface of the monovalent oxide Cu<sub>2</sub>O.

At higher redoxpotential Kuntze et al.<sup>31</sup> has shown in detail that an amorphous copper hydroxide (some nm in thickness) is formed with a growing copper oxide layer underneath it.

Our studies from neutral waters and the investigations above in alkaline solutions indicate that a monovalent hydroxide Cu(OH) should be included in the Pourbaix diagram for copper<sup>32</sup>, this is indicated in Figure 1.

The Pourbaix diagram in Figure 1 does not contain chlorides but the combination of chloride and sulphide is known to be detrimental and cause localised corrosion, such as pitting<sup>33,34</sup> intergranular corrosion (IGC)<sup>35</sup> and stress corrosion cracking and SCC<sup>36</sup>

In a recent study of F.M. Al Kharafi et al.<sup>35</sup> it was stated: ”This paper documents the occurrence of sulphide-induced IGC of copper in salt water. The process is shown to be rapid, being discernible within some tens of minutes. The present results are immediately relevant to the discussion of the proposed use of copper canisters for the disposal of Swedish, Finnish, and Canadian high-level nuclear waste deep in granite environment”

Studies by W. Liu et al.<sup>37</sup> in hydrothermal solutions/groundwater concludes that copper solubility “shows systematic increases with increasing temperature” and “chloride

concentration”. “For sediment-hosted copper deposits, usually formed at low temperature, copper chloride complexes are thought to be important for copper transport.” However, these processes are not well understood mainly “due to the lack of reliable copper (I)-chloride complexing data”. The copper(I) chloride complex,  $\text{CuCl}^{2-}$ , is likely to be most important species for transporting copper in sedimentary basin and brines, although at lower chlorine concentrations (at around 50°C),  $\text{CuCl}_3^{2-}$  is likely to become important.

The formation of  $\text{CuCl}^{2-}$  complexes at lower redox potentials in groundwater is also pointed out in the SKI report 99:52<sup>33</sup>, see page 56. Furthermore, it is stated on page 60 that “the immunity of copper decreases as the chloride and sulphide concentrations increase. This results in a dangerous situation with low immunity of copper and complex copper sulphide film of variable and disputable ability to passivate.”

In a calculation in Ref. 38 of the system Cu-Cl-S-C-H-O (Fig. E5, page 105) with low  $\text{Cl}^-$  and low  $\text{HS}^-$  and high carbonate ion concentrations compared to the Swedish groundwater, a small region for immune copper metal was theoretically predicted. A similar calculation with low  $\text{HS}^-$  (and quite low  $\text{Cl}^-$ ) and high carbonate ion concentrations is also shown in Fig. 18 (page 65). The  $\text{Cl}^-$  concentration in the Swedish groundwater at 500 m depth could easily reach 12-15000 ppm, see CRIEPI-report<sup>39</sup>.

It would of course be interesting to make such calculations with the expected ion-concentrations in a repository, although the thermodynamic databases are still incomplete regarding monovalent chloride complexes, monovalent hydroxides and copper ion solubility, especially at elevated temperatures.

All in all it may be concluded that there is no copper immunity area in the experimental Pourbaix diagram for the system copper/ Swedish groundwater containing sulphides and chlorides. This is supported by the fact that no native copper is found in the Swedish bedrock/groundwater.

As discussed earlier, native copper is found in some few places in the earths crust and the nearest position to Sweden is probably southwest of Finland where microscopic grains of metallic copper is found in pegmatite veins in precambrian crystalline rock<sup>38</sup>

During anoxic conditions in nature the formation of  $\text{CuOH}$  is probably present but not dominating, since more stable products containing sulphide or chloride is thermodynamically favoured. However in a situation far from equilibrium, such as a repository with copper metal and bentonite clay, a local depletion of ions like sulphide and chloride might take place and then both copper hydroxides and copper oxides may form. The thermodynamic final state for copper in the Swedish groundwater is most probably copper sulphides but depending on the local chemistry, the reaction path could go via chloride complexes, hydroxides and oxides. It can be concluded that there is no thermodynamic “copper immunity area” in the practical Pourbaix-diagram within the expected Swedish repository environment.

## **PART 2: DISCUSSION REGARDING THE BRITE-REPORT**

The BRITE-group has asked us to make a simple mass-balance calculation based on the main experiment, the “Pressure gauge experiment”, see page C64 in Ref. 2.

The mass-balance calculation shows that it is possible to fully match the total amount of released hydrogen in the system to the calculated amount of formed corrosion product, see Appendix 1.

We have not measured the amount of copper in the water in this specific "Pressure gauge experiment", however this was done in an earlier study and found to be 0.5 mg/dm<sup>3</sup> at room temperature<sup>40</sup>. The amount of copper ions in the water is not included in the mass-balance calculation but it would of course contribute to the total amount of corrosion and corrosion rate, especially since the solubility of copper is expected to be much higher at elevated temperatures.

***Alternative hypotheses to the observed hydrogen evolution are discussed in Chapter 2.2.***

Alternative hypothesis 2-4, for hydrogen formation has been proposed by the BRITE-group, which are commented below.

**Hypothesis 2:** The anodic reaction would possibly be that of oxidation of a pre-existing Cu(I)- to Cu(II)-oxide (e.g. Cu<sub>2</sub>O to Cu(OH)<sub>2</sub>) via e.g. the summary reaction:  
$$\text{Cu}_2\text{O} + 3\text{H}_2\text{O} = 2\text{Cu(OH)}_2 + \text{H}_2$$

- Comment: One obvious problem with this reaction is that if a monovalent product (Cu<sub>2</sub>O) is formed during the oxic part of the exposure and that this product converts into a bivalent product during the anoxic part of the exposure, then the bivalent hydroxide must be more stable. This would need a revision of the known thermodynamics. If it would be true, that a bivalent hydroxide Cu(OH)<sub>2</sub> is stable in equilibrium with H<sub>2</sub> in the millibar range, it would implicate even more serious corrosion problems for copper in contact with (anoxic) water.

**Hypothesis 3:** Water always contains H<sup>+</sup> and OH<sup>-</sup> ions, formed by natural dissociation. One hypothesis is that the recombination of H<sup>+</sup> from water dissociation is catalysed by the copper surface giving rise to hydrogen gas generation. Here the anodic reaction could be e.g. oxidation of dissolved Cu<sup>+</sup> to Cu<sup>2+</sup> in the water (Cu<sup>+</sup> dissolved earlier during oxide growth in presence of remaining oxygen), or oxidation of hydroxide ions,  $4\text{OH}^- = \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$  (the latter would require a high potential, which is not impossible but considered unlikely).

- Comment: Same problem here as in hypothesis 2, a monovalent ion is supposed to dominate the oxic exposure and a bivalent ion the anoxic exposure. The result would be Cu<sup>2+</sup> and OH<sup>-</sup>, i.e. the same situation as in Hypothesis 2.

**Hypothesis 4:** Hydrogen gas is formed from hydrogen left in the copper as a result of the manufacturing process.

- Comment: This is discussed in Appendix 1, the mass-balance calculation. The hydrogen content in the foils from Johnson-Matthey was around 1 wtppm in as delivered condition and around 5 wtppm after the exposure (Pressure gauge experiment).

***The chapters “2.3 Thermodynamic perspectives”, and “2.9 Solid phase analysis”***

These topics are dealt with in our latest publication which was published after the release of the BRITE- report. In perspective of our new thermodynamic findings regarding Cu(OH), these chapters are not relevant any more. We refer here directly to our publication in Catal. Lett.<sup>15</sup>.

***Comments to the chapters “2.4 Reaction rate estimations”, “2.5 Amount of hydrogen generated”, “2.6 Apparent activation energy” and “2.8 Copper metal as a hydrogen source”***

The BRITE-group has made estimates of the corrosion rates and activation energies based on the hydrogen pressure measurements, see Chapters 2.4-2.6. We have pointed out that it is more or less pointless to do such calculations/estimates, due to the following reasons:

- Our experiments are not designed to determine the corrosion rate but the sole purpose is to show that copper corrodes under slow hydrogen evolution i.e. that copper on the whole reacts with water molecules.

- It is only a minor part of the hydrogen that is found in the gas phase. The gas pressure that is measured above the palladium membrane consists of only 1 – 20% of the total hydrogen released due to copper corrosion (changes with the experimental parameters such as exposure time, temperature, the amount and thickness of Cu, the amount of water and gas phase and the dimensions of palladium membrane, etc.). A considerable portion of the hydrogen remains in the copper metal as well as in the corrosion product. This means that continuous hydrogen charging of the metal occurs due to anoxic corrosion. A significant portion of hydrogen is also found in the palladium membrane. Moreover a certain hydrogen leakage always occurs even in UHV-compatible components. In other words, the measured rate of hydrogen release is not at all the same as the corrosion rate.

- Changed composition and less protective/passivating properties of the product with time. The corrosion rate is very low during the first months and it is dependent on that copper initially builds a somewhat protective oxide film in the presence of dissolved oxygen in the water. When the dissolved oxygen in the water is consumed, a slow transformation of the oxide film to a porous complex corrosion product is expected that contains high amount of hydrogen and hydroxide.

- Hydrogen charging results in a more defective product. Hydrogen charging of the copper metal due to corrosion is very slow but hydrogen charged metal, including copper, displays a higher corrosion rate, probably due to formation of a more defective and “protonated” corrosion product<sup>15</sup>. That is to say that a thick copper plate will corrode more slowly compared with thin foils under the initial hydrogen-charging period. A five cm thick copper wall might easily have an “initial” hydrogen charging period of several years and consequently a lower corrosion rate

- Successively, as the hydrogen gas pressure comes close to the equilibrium pressure, the corrosion rate decreases (Pressure gauge experiment).



If corrosion rate estimation should be performed anyway, knowing about the severe uncertainties as discussed above, a rough attempt is done here for the “Pressure gauge experiment”. It is likely that a somewhat passivating oxide surface layer is formed during the initial oxic period of 1200h and the fact that under the following anoxic exposure with increasing hydrogen pressure towards equilibrium it might be reasonable to use a shorter “effective” anoxic exposure time in the estimation, for example around 400h. Assuming that the monovalent oxide is still the dominating product, as in the mass balance calculation above,  $2 \times 4.25 \times 10^{-5}$  mole Cu or  $5.4 \times 10^{-3}$  g Cu has corroded under the anoxic exposure.  $5.4 \times 10^{-3}$  g Cu/ $150 \text{ cm}^2$ / 400h give roughly a corrosion rate of  $1 \text{ }\mu\text{m/year}$ , which is in the same order of magnitude as observed in copper cooling systems as discussed above.

### ***The Chapters 3-5***

We have not been asked to make any specific comments on these Chapters, but nevertheless some of these topics are at least partially discussed in this report, for example the natural analogues with native copper, thermodynamic immunity in Swedish groundwater and briefly possible consequences on KBS-3.

## **General comments and conclusions**

- Detection of hydrogen in the gas phase, corrosion product and in the copper metal in several different anoxic water exposures represents strong evidence for anoxic copper corrosion in pure water.
- Hydrogen in the copper metal, after removal of the corrosion product, has been detected with thermal degassing (up to  $700^\circ\text{C}$ ) equipment coupled to a mass-spectrometer as well as with SIMS-analysis. The hydrogen content in unexposed Cu was typically 1 wtppm and after exposure typically in the range of 5-30 wt-ppm.
- Copper do react with water molecules and it is shown experimentally by us and other research groups. It is thermodynamically supported by first principle calculations by two independent research groups that copper do split/react with water.
- The alternative hypothesis 2-3, suggested by the BRITE-group does require revision of known thermodynamics regarding copper corrosion whereas our findings (CuOH) represent only an addition to known thermodynamics.
- In anoxic environments at low redoxpotentials the first corrosion product formed on a copper surface is a monovalent amorphous hydroxide. At somewhat higher potentials (still anoxic) a bivalent amorphous hydroxide is formed. Under the initially formed hydroxide, copper oxides may form.
- The thermodynamics regarding copper corrosion in pure anoxic water is incomplete, both regarding copper solubility and formation of monovalent corrosion products such as CuOH. Copper corrosion by pure water is very temperature sensitive and there is a surprisingly large lack of knowledge regarding copper corrosion, especially in hot water. This incompleteness is evidenced by the fact that copper does corrode by water

in cooling systems. Irrespective of water chemistry (pure, degassed water), the corrosion rate is in the 0.5-10  $\mu\text{m}/\text{year}$  range at 40°-70°C.

- The thermodynamics regarding copper corrosion in anoxic groundwater is even more incomplete, for instance regarding the formation of monovalent copper chloride products and complexes.
- An important fact is that anoxic copper corrosion, especially when the metal is exposed to an anoxic environment on both sides, results in hydrogen charging which is detrimental for the mechanical properties<sup>14,43</sup> and might result in hydrogen embrittlement<sup>44</sup>.
- During anoxic conditions in nature the formation of CuOH is probably present but not dominating, since more stable products containing sulphide or chloride is thermodynamically favoured.
- Newly published results show that not only pitting corrosion but also IGC and SCC occur on copper in groundwater environments.

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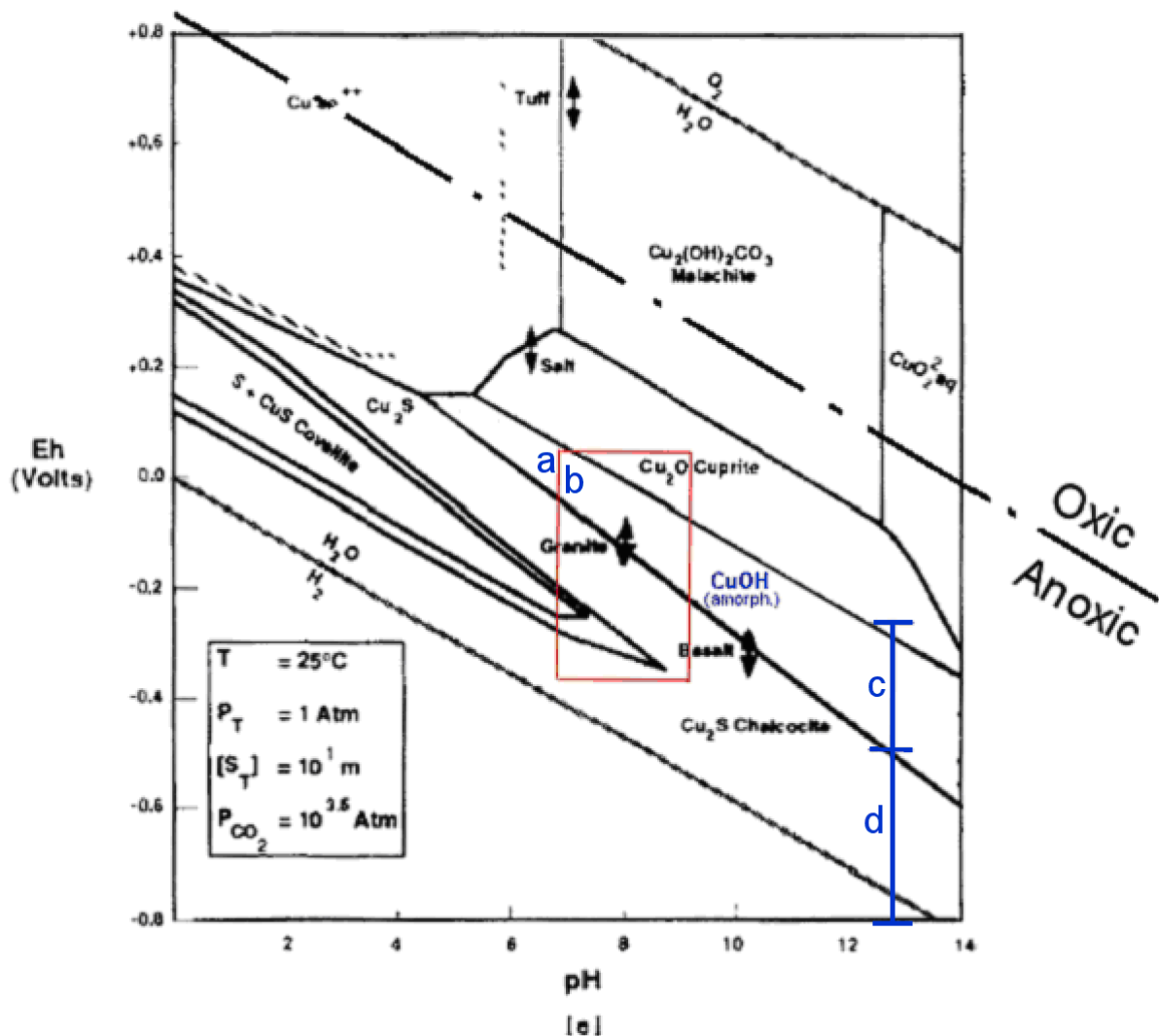
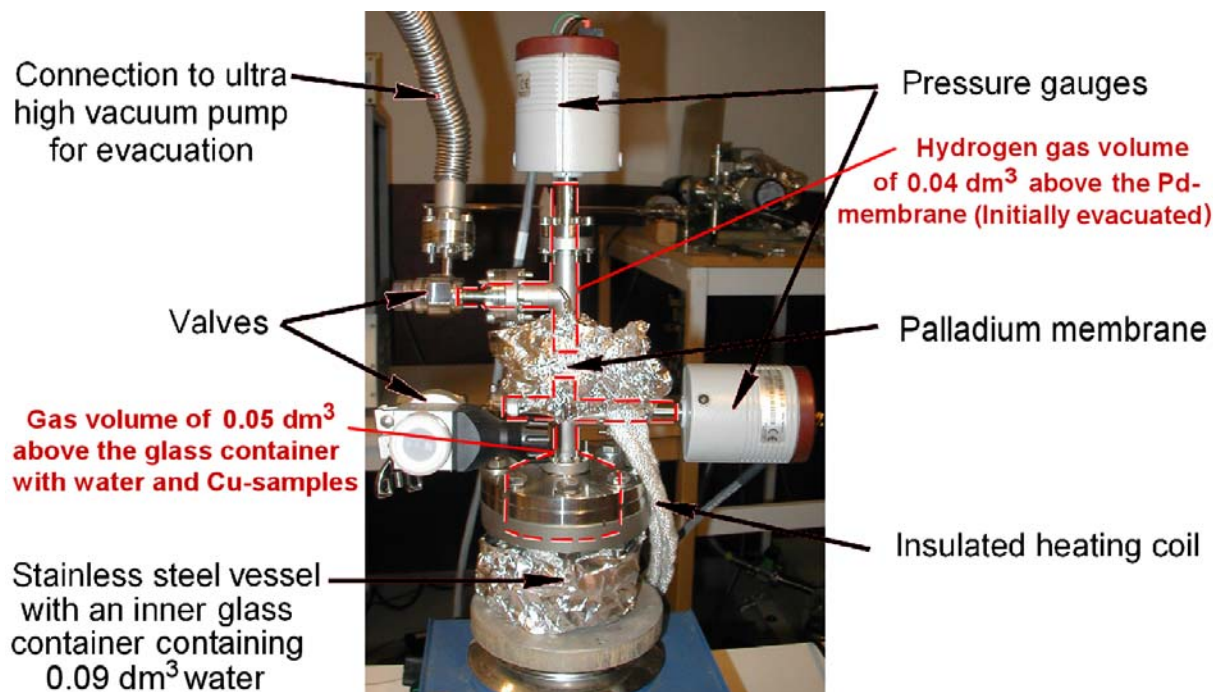


Figure 1. Potential-pH diagram for phases in the Cu-H<sub>2</sub>O-S-CO<sub>2</sub> system<sup>32</sup>. The borderline between oxic and anoxic environment is indicated and it corresponds to a gas phase with a total pressure of 10<sup>-28</sup> bar. Cu(OH) is introduced based on the Refs. 14,15,18 and 30, marked with a-d. Red rectangle shows the expected environment in a repository environment, albeit chlorides are excluded. If monovalent chloride-compounds such as CuCl<sup>2-</sup> and CuCl<sub>3</sub><sup>2-</sup><sup>33,37</sup> are introduced in the same diagram, which are present in groundwater, these compounds will also be expected in the region of monovalent CuOH. Obviously, there will not be any region with stable Cu-metal in the practical Pourbaix diagram regarding the Swedish repository environment. This is supported by the fact that no native copper is found in the Swedish bedrock/groundwater.

## Mass balance calculation

The calculation based on the "Pressure gauge experiment", see page C64 in Ref. 2.



Experimental set-up, Figure 1 in Ref 2.

### Start condition:

Temperature:  $22^\circ \text{C}$

Amount of copper: 13.087 gram with a water exposed surface of around  $150 \text{ cm}^2$ .

Amount of water:  $0.09 \text{ dm}^3$

Gas volume above the water (under the Pd-membrane):  $0.05 \text{ dm}^3$

Gas volume above the Pd-membrane:  $0.04 \text{ dm}^3$  (Initially evacuated)

After evacuation of all air above the water, a new effective gas equilibrium was reached within about 48 hours:

12.5 mbar  $\text{O}_2$ -gas or  $5.14\text{E-}5 \text{ mol oxygen (O)}$

47 mbar  $\text{N}_2$ - gas

28 mbar  $\text{H}_2\text{O}$ -gas

### **A possible mass-balance calculation (no error bars, just to demonstrate that the numbers are roughly correct:**

The corresponding hydrogen pressure in the whole system may be summarized to:  $1.25+0.25 = 1.5 \text{ mbar}$ , which gives  $4.59\text{E-}6 \text{ mol H}_2\text{-gas}$ . The amount hydrogen charging (increase) in the copper metal due to anoxic water corrosion is estimated to be around 4 wppm. The hydrogen content in the foils in as delivered condition is typically around 1 wppm (Based on thermal gas desorption up to  $500^\circ\text{C}$  before and after the exposure). This corresponds to an increase of  $5.24\text{E-}5 \text{ mol hydrogen (H) in the metal}$ .

Estimation of the amount of hydrogen in the corrosion product: The total weight gain of 1.5 mg is approximated to come only from oxygen (***9.38E-5 mol O***), i.e. the weight gain due to hydrogen uptake in the copper is neglected. Since the product contains oxides and hydroxides we can for instance calculate with  $\frac{3}{4}$  Cu<sub>2</sub>O and  $\frac{1}{4}$  CuOH which gives the following amount of elements in the mixed corrosion product:

O	9.38E-05	mol
H	2.34E-05	mol
Cu	1.64E-04	mol

Since the product is porous we assume that the effective density is no more 3 g/cm<sup>3</sup> which give a thickness of about 0.6 μm.

The total amount of released hydrogen from water molecules, calculated as gas, H<sub>2</sub>, is thus: ***4.25E-5 mol*** (Gas phase:0.459E-5 +copper metal:5.24E-5/2 +product:2.34E-5/2). The amount of released and consumed oxygen (O) from water molecules is of course the same, ***4.25E-5 mol***. This should be added to the initial amount of oxygen gas (5.14E-5 mol O) which gives the ***total amount of consumed oxygen: 9.39E-5 mol O***.

This mass-balance shows that it is possible to fully match the total amount of released hydrogen in the system to the calculated amount of formed corrosion product since the weight gain measurement gave almost the same result: ***9.38E-5 mol oxygen (O)***.