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Will Copper Canisters Contain Nuclear Waste for 100K Years?

New Research Ideas Forum – June Meeting

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Introduction

- The final disposition of high level nuclear waste (i.e., used nuclear fuel) is an issue which plagues all nuclear nations
- Irrespective of whether used fuel is stored intact, or if it is reprocessed, there is a volume of long lived radionuclides which must be disposed of
- Geologic disposal is required

Introduction

- Repository design generally consists of a series of natural and engineered barriers.
- Storage container often plays a primary role in waste confinement
  - Corrosion resistant containers
  - Corrosion allowance containers

Why Copper?

- Cu containers have been proposed for a number of proposed repositories
  - Sweden
  - Finland
  - Canada
  - Japan
  - Switzerland (their alternate design for longer times)
- Similar geologic conditions
  - Saturated, granitic formations
  - Copper container inside clay buffer
- Why have they been proposed
  - Natural analogs
  - artifacts

The Swedish KBS-3 Repository Design

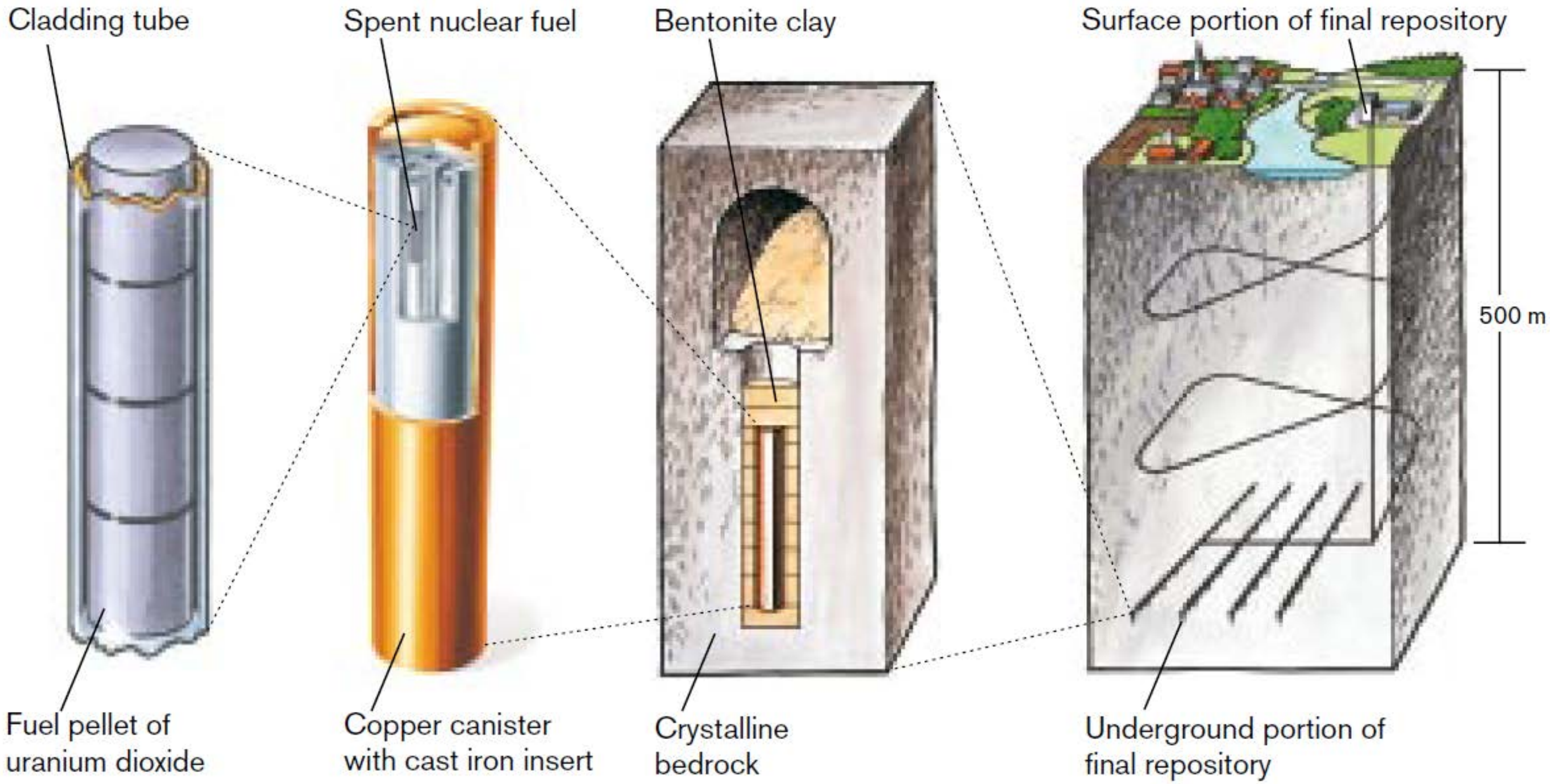
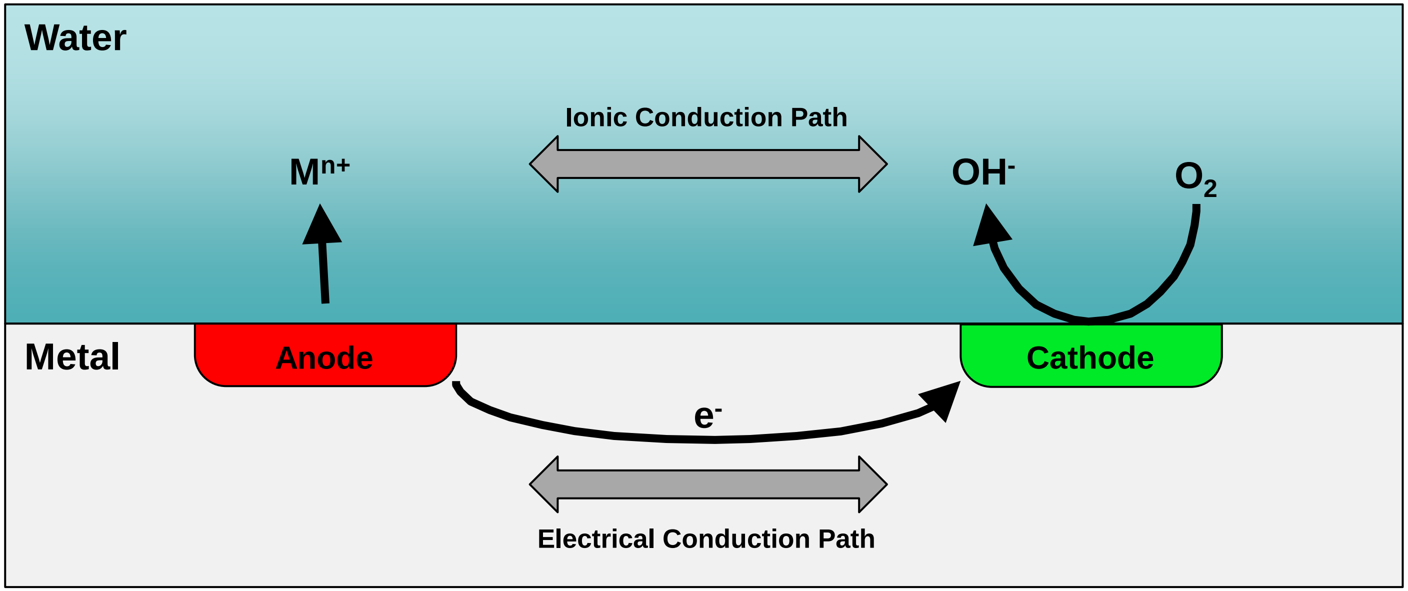


Figure 1. *The KBS-3 concept for disposal of spent nuclear fuel.*

From SKB 2006 "*Long-term Safety for KBS-3 Repositories at Forsmark and Laxemar*", TR-06-09

The Basics of Corrosion

- In order for a corrosion reaction to take place, four things are needed:
  - Anode (where oxidation takes place)
  - Cathode (where reduction takes place)
  - Electrical conduction path (anode and cathode must be electrically connected)
  - Ionic conduction path (to close the loop)



Thermodynamics of Corrosion

- Potential-pH diagrams (Pourbaix diagrams) are a representation of the various possible reactions – sort of an electrochemical phase diagram

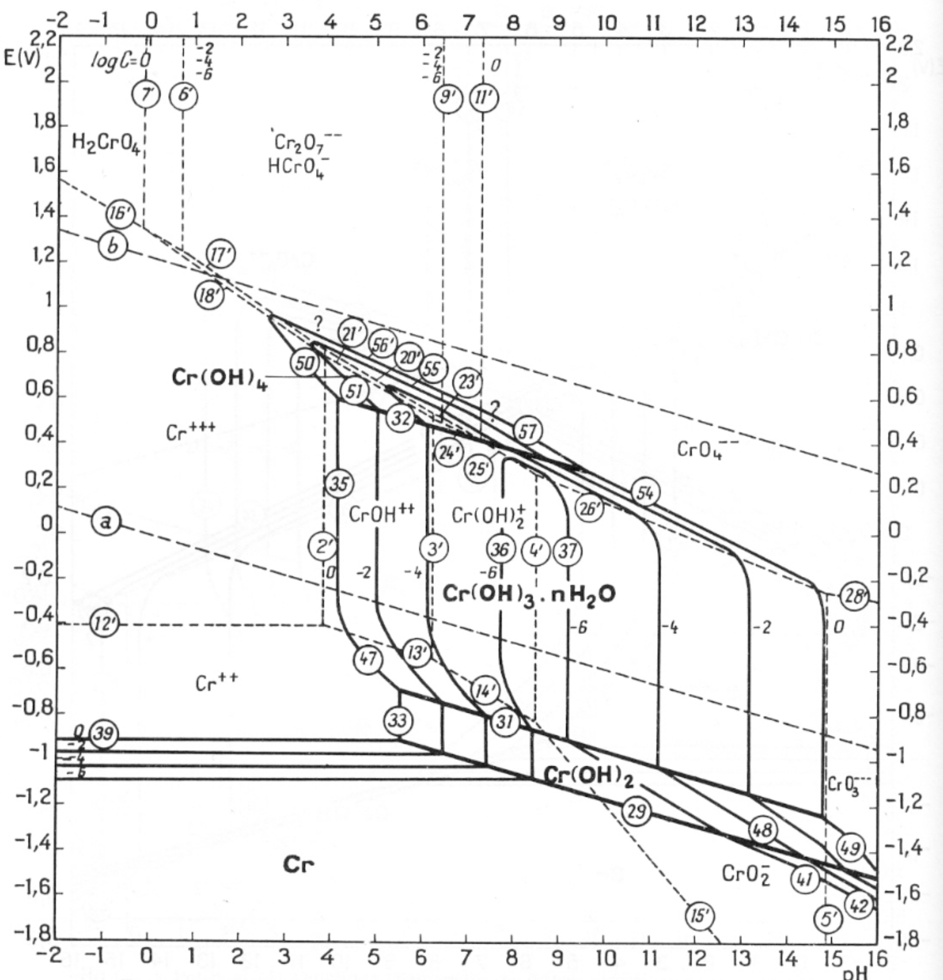


FIG. 4. Potential–pH equilibrium diagram for the system chromium–water, at 25°C. In solutions containing chloride. [Approximate representation made by considering $Cr(OH)_3.nH_2O$.]

- Chemical and electrochemical reactions considered (for which there is thermodynamic data)
- Only consider the element and water (modified diagrams do exist considering pertinent aggressive species such as sulfide or chloride)
- These are thermodynamic diagrams – they do not tell us kinetics
- Region of stability of water is indicated (a and b lines)

The Cu-H_2O Pourbaix Diagram

- Copper in water differs from the previous diagram for Cr in that metallic copper is thermodynamically stable at much higher potentials

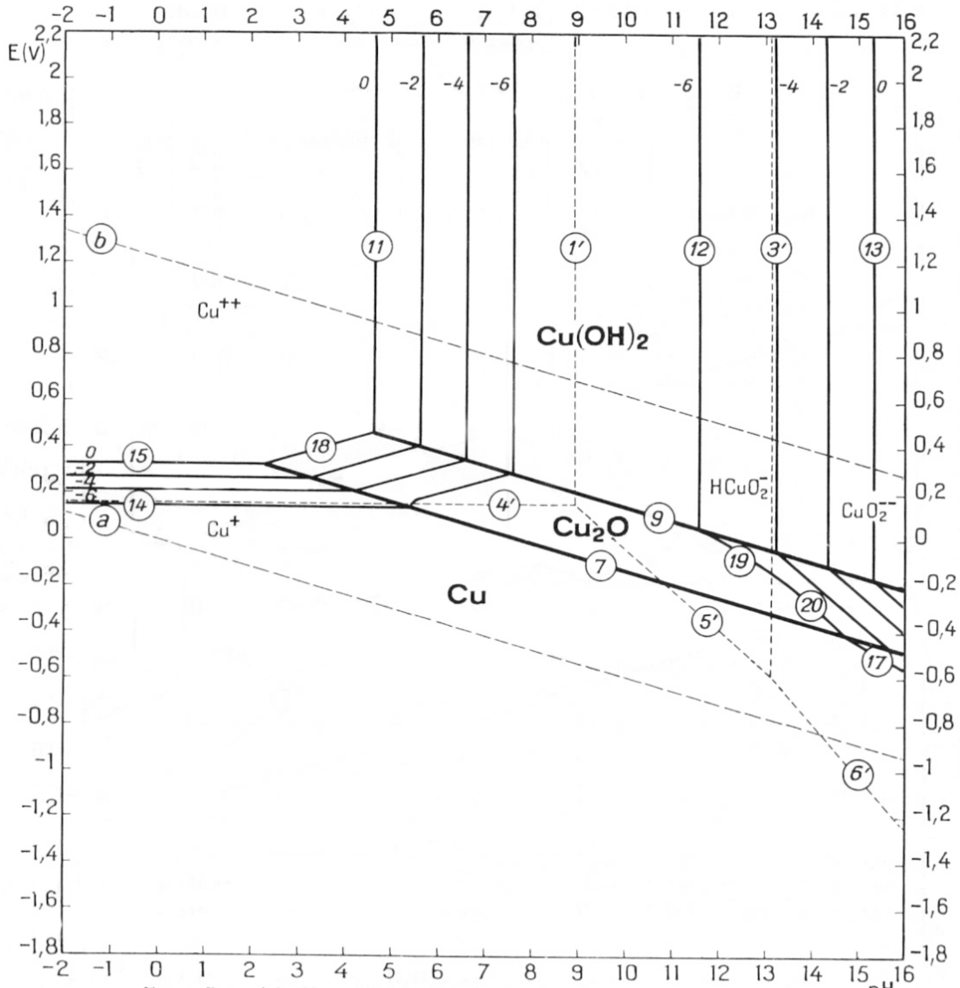


FIG. 2. Potential-pH equilibrium diagram for the system copper-water, at 25°C. [Considering the solid substances Cu, Cu_2O and $Cu(OH)_2$. CuO is not considered.]

- Metallic copper is stable at potentials more positive than the a line for water reduction.
- Metallic copper is predicted to be thermodynamically stable in the absence of dissolved oxygen as there is no viable cathodic reaction to support oxidation.
- A limitation of this diagram is that it considers only the species for which thermodynamic data exists – metastable species are not considered, nor are species that have not yet been identified experimentally (this becomes important later…)

Should copper corrode in anoxic water?

- Traditional explanation – No!
- No viable cathodic reaction
  - No dissolved oxygen = no oxygen reduction
  - Water reduction is not thermodynamically viable
- Are there conditions where the dissolved oxygen content is zero, but copper can still corrode?

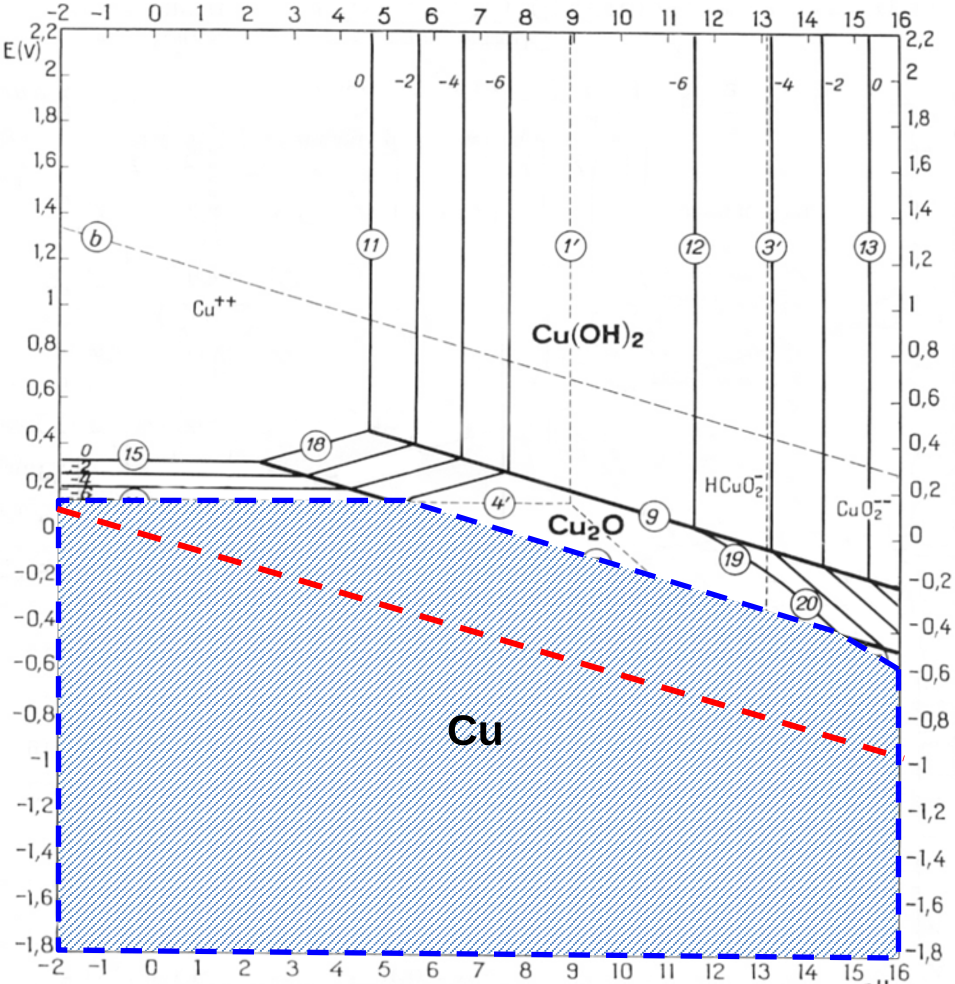
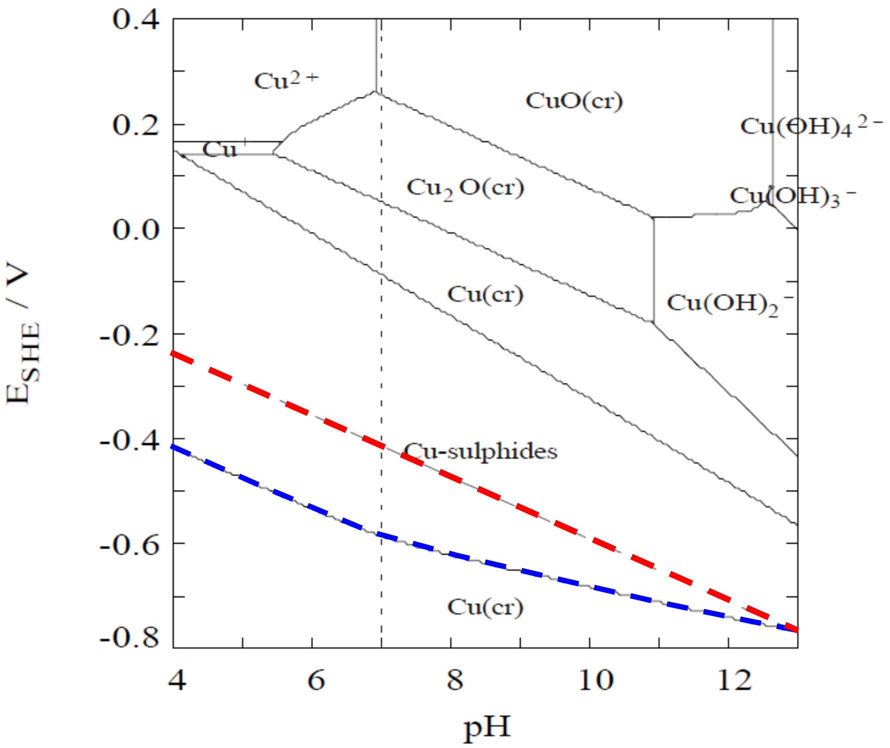


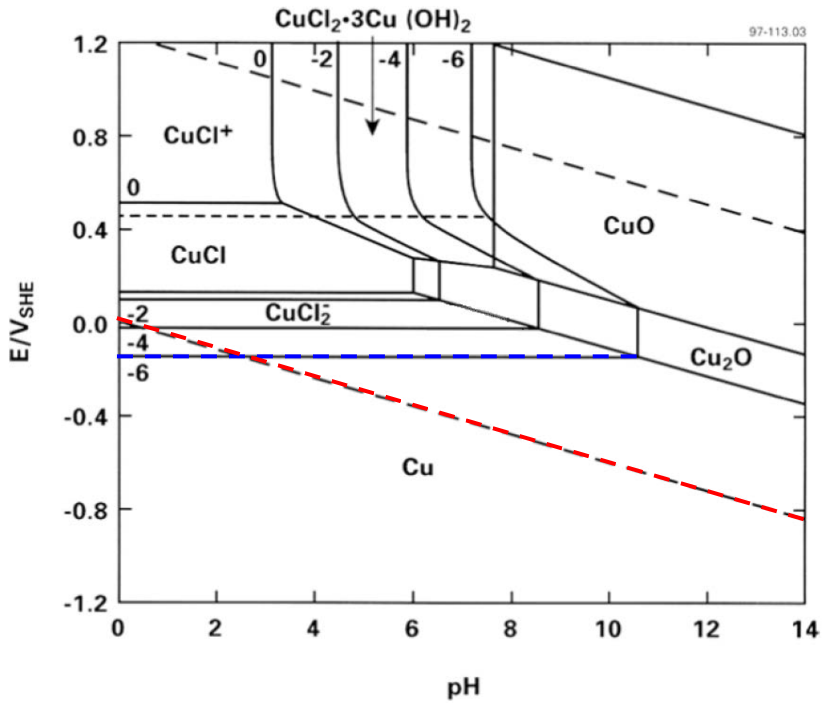
FIG. 2. Potential-pH equilibrium diagram for the system copper-water, at 25°C. [Considering the solid substances Cu, Cu_2O and $Cu(OH)_2$. CuO is not considered.]

Is copper corrosion resistant in all deaerated, aqueous solutions?

- Sulfide containing solutions are very aggressive towards copper
- Chloride solutions are aggressive at low pH
- Other ions (ammonia, phosphate, etc.) do not result in the same effect



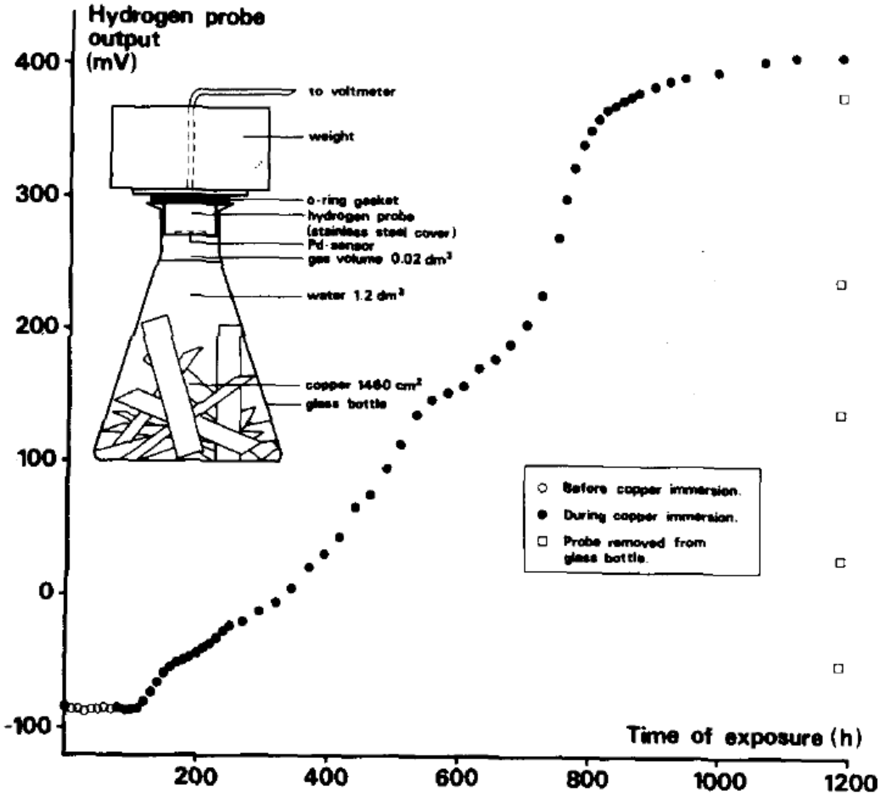
Puigdomenech, 2000 (SKB Report TR-00-13, “Thermodynamic Data for Copper”)



King, 2010 (SKB Report TR-10-69, “Critical Review of the Literature on the Corrosion of Copper by Water”)

Despite the thermodynamics, has corrosion been experimentally observed?

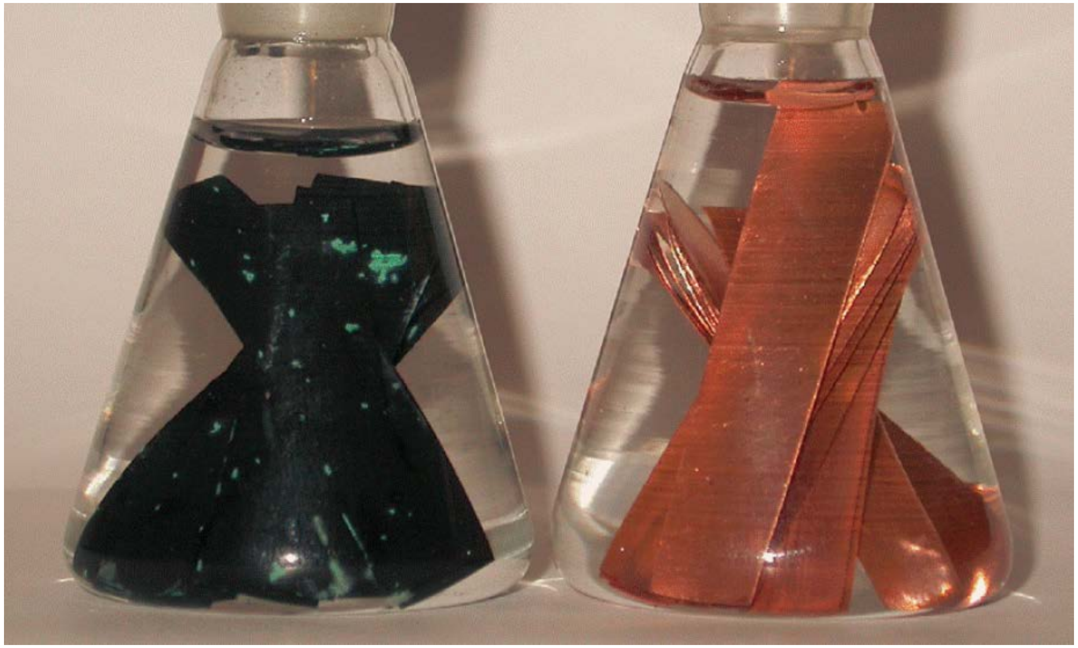
- In 1986, Hultquist published results suggesting that corrosion of copper did occur in anoxic water.
- A hydrogen probe was used to measure the gas in a region separated from the test solution headspace by a Pd foil
- Weight change (gain) observed on copper coupons
- Subsequent papers by others demonstrated that the probe was likely drifting/unstable over such a long time period.

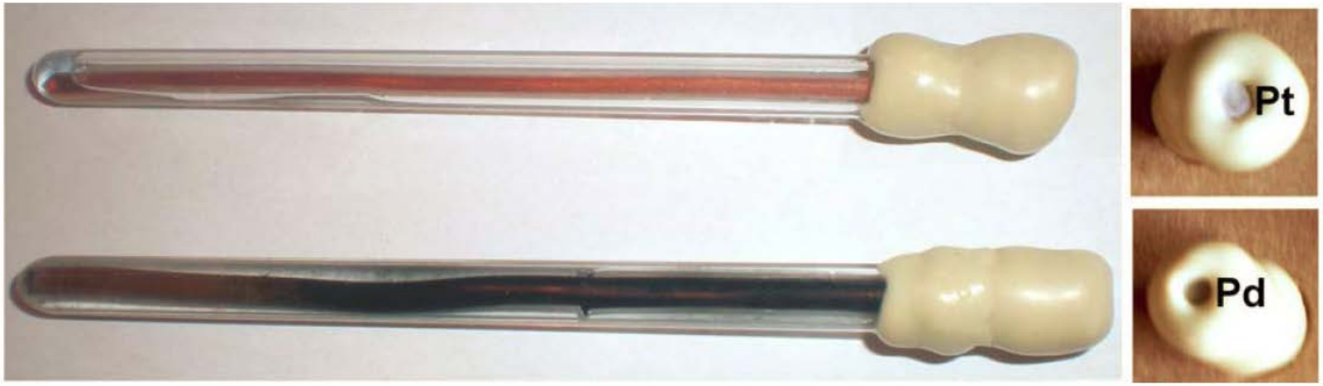


Hultquist, Corrosion Science, Vol. 26, No. 2, pp. 173-177, 1986

Despite the thermodynamics, has corrosion been experimentally observed?

- Cu sheet placed in high purity water and sealed for a period of 15 years
- Left container had a Pd membrane as part of the seal while right container was all glass
- Hydrogen containing corrosion product identified on the metal surface
- Claimed high hydrogen content in Cu (as much as 40 wtppm)

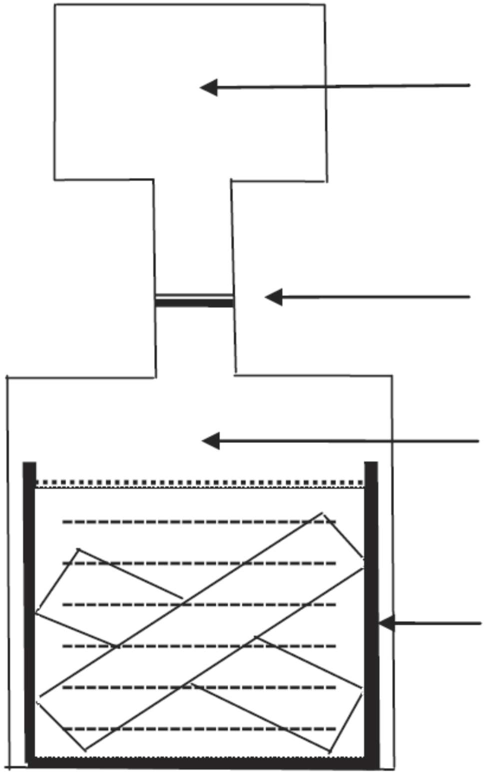




Hultquist, et al. 17th International Corrosion Congress, Paper no. 3884, 2008

Evaluating gas evolution from Cu in anoxic water

- Similar configuration to the 1986 paper with Cu in high purity water



Initially evacuated 60 cm^3 volume with two absolute pressure meters and, via a leak valve, connected to a mass spectrometer in Ultra high vacuum for verification of hydrogen

Palladium foil, ∅ 16 mm, nominal thickness,100 µm
~3 cm^2 between upper and lower volume
~0.03 cm^2 in hydrogen contact with air

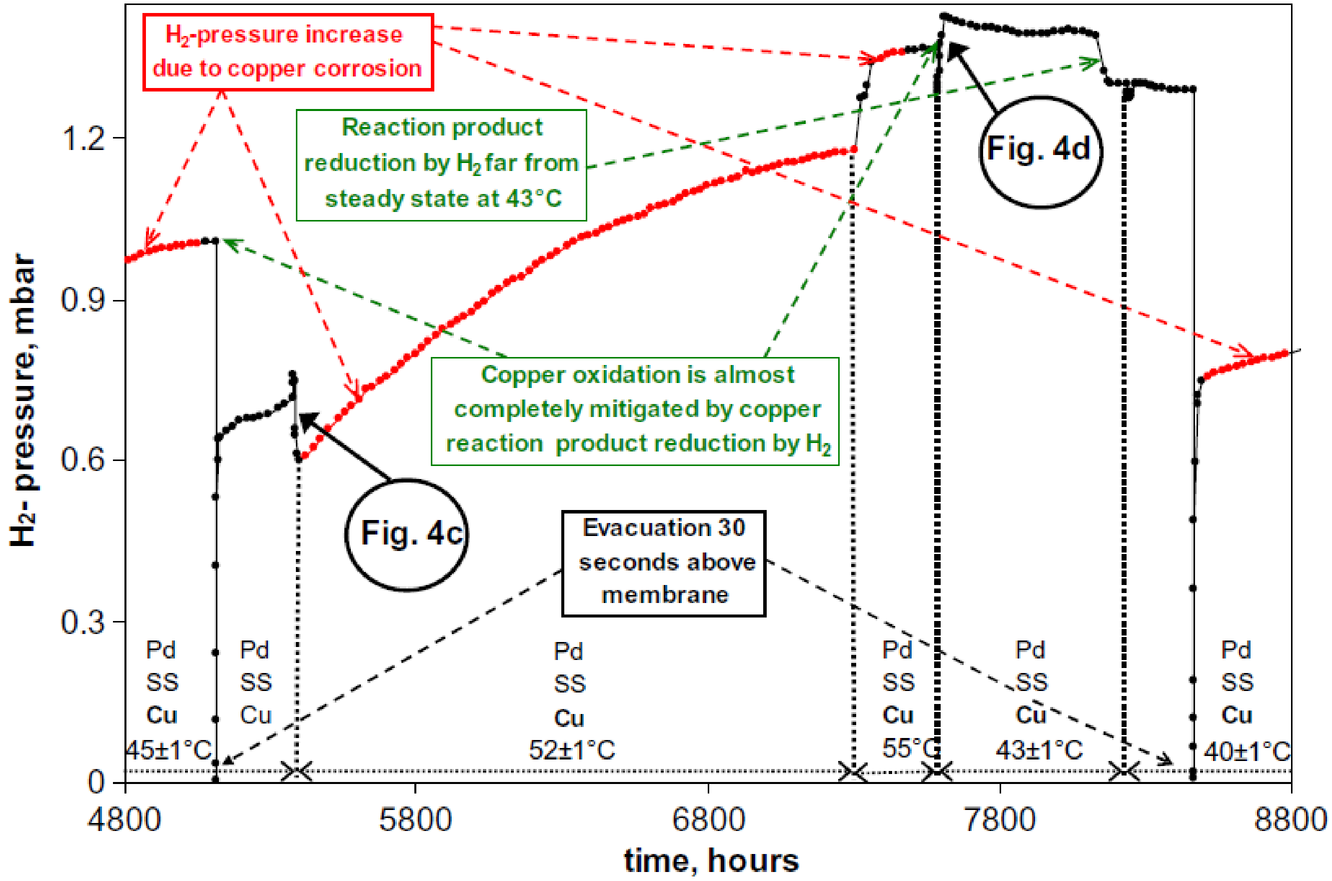
60 cm^3 gas volume with an absolute pressure meter and valve for evacuation

Soda glass container with 90 cm^3 liquid water and immersed approximately 140 cm^2, 99.95%, copper sheets with thickness 0.1 mm

Hultquist, et al. Corrosion Science Vol. 53 (2011), pp. 310-319.

Evaluating gas evolution from Cu in anoxic water

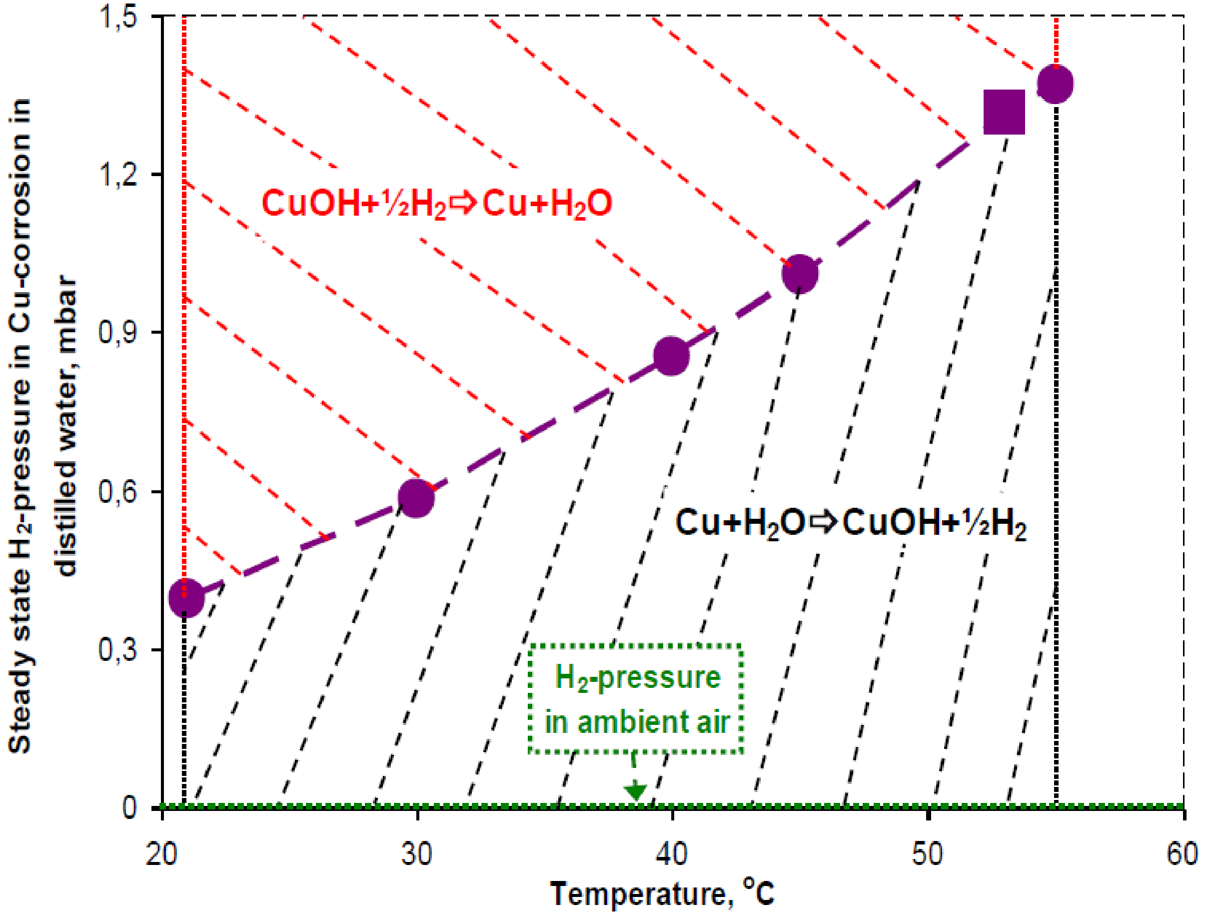
- Gas pressure measured as a function of time and exposure temperature



Hultquist, et al. Corrosion Science Vol. 53 (2011), pp. 310-319.

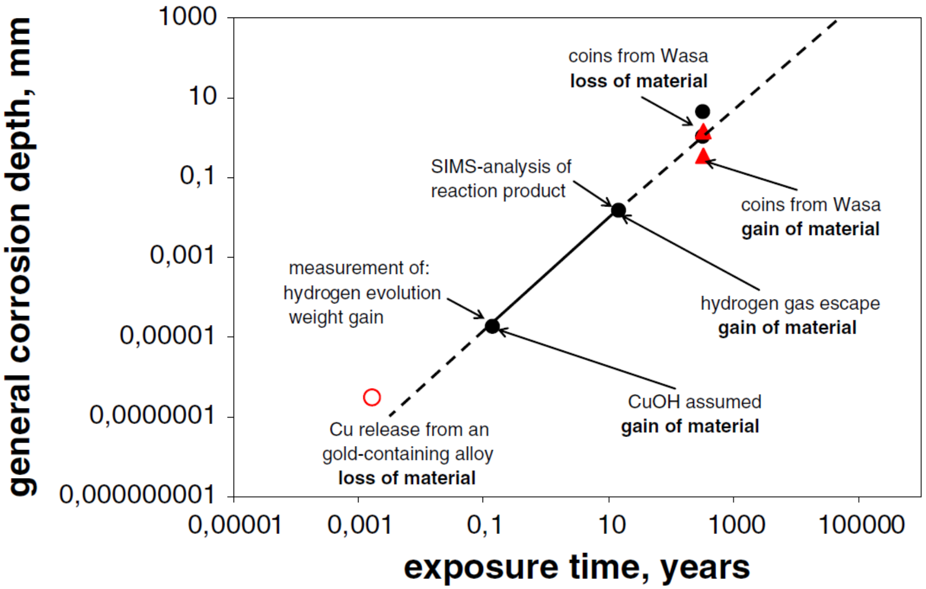
Hultquist – Present explanation/theory

- Cu reacts with water producing H as a by-product
- H can be detected in the Cu metal from the reaction between Cu and H_2O
- A solid reaction product (CuOH) is formed on the Cu surface



Hultquist, et al. 2013, Strål Säkerhets Myndigheten, Report number: 2013:07

Implications of Hultquist's Data



From Hultquist et al., 2009

- By linking together exposures with widely varying durations of copper to liquid water without or negligible O_2, 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.

But…

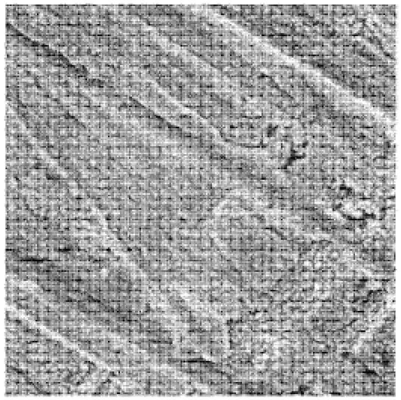
- Widely varying exposure conditions
- Extrapolating on a log-log plot…

Concerns with Hultquist’s claims

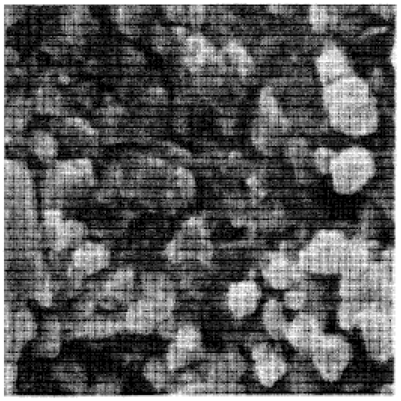
- No published attempts to replicate Hultquist’s data have been successful.
- Corrosion product claimed by Hultquist has not been observed experimentally by anyone, including Hultquist
- Hydrogen contents claimed in the Cu metal are far beyond the solid solubility in Cu

Attempts to Replicate Hultquist’s Results

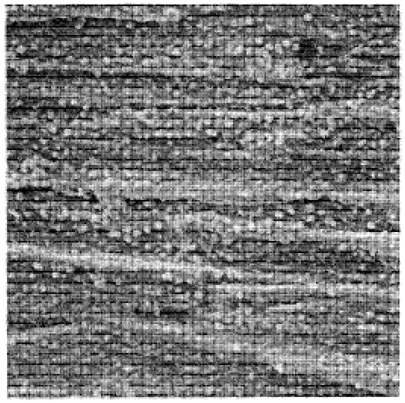
- Möller attempted to replicate the experiment in the glass tubes (with a Pd or Pt membrane)
- No difference observed after 2 years when comparing the two
- No oxide growth after the first year



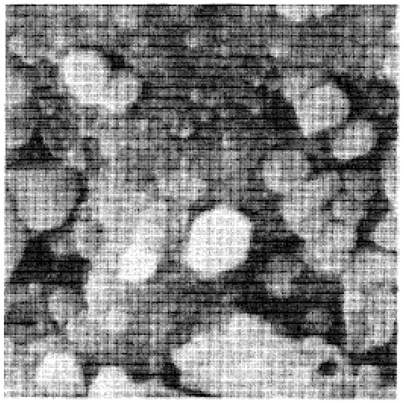
Figur 6a. SEM-fotografi på oxidskiktet på Cu-bleck från Pt-förslutning. Förstoring 2000X



Figur 6b. Samma som (a) men med förstoringen 20 000X



Figur 7a. SEM-fotografi på oxidskiktet på Cu-bleck från Pd-förslutning. Förstoring 2000X

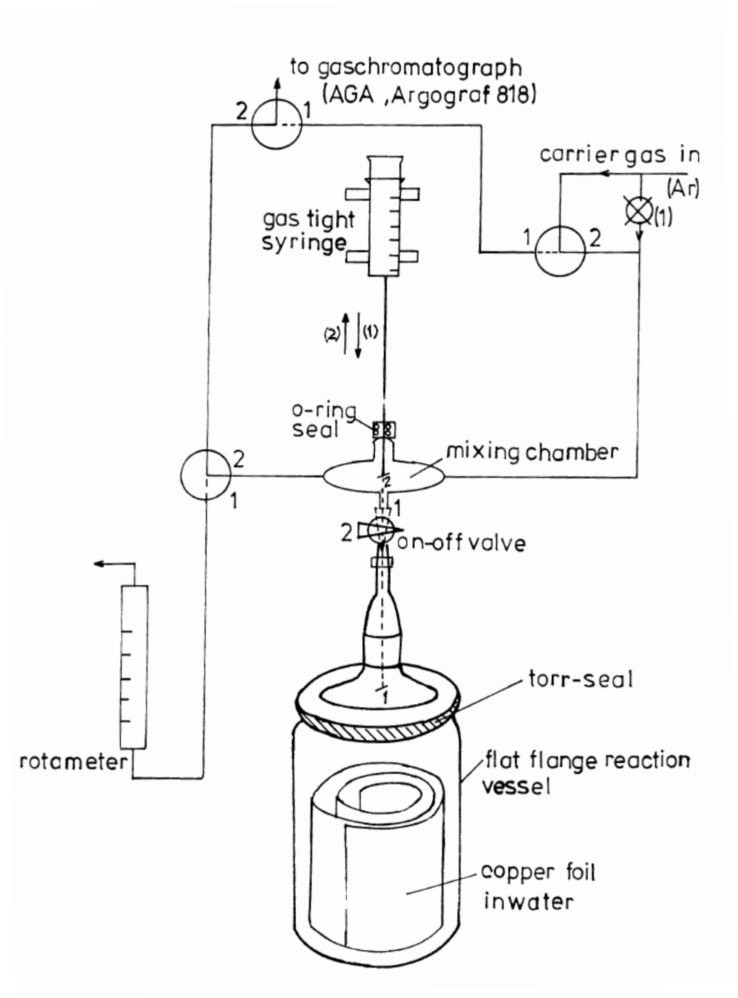


Figur 7b. Samma som (a) men med förstoringen 20 000X

Pt membrane

Pd membrane

Attempts to replicate Hultquist's results



- Eriksen et al. (1988, 1989)
- Cu foil placed in deaerated, high purity water for a period of 61 days
- No hydrogen evolution was detected (detection limit of 10ppm)
  - Leak-tightness of system verified via a 12 day experiment with a 100ppm gas sample where no loss was observed
- XPS analyses of surfaces found only Cu_2O as the corrosion product

Attempts to replicate Hultquist’s results

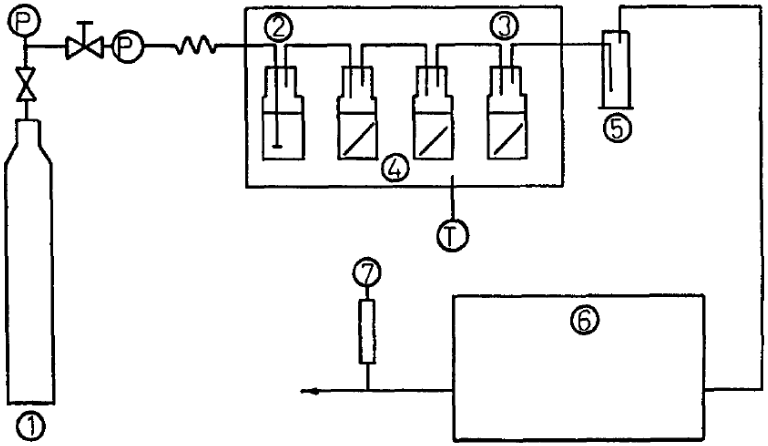


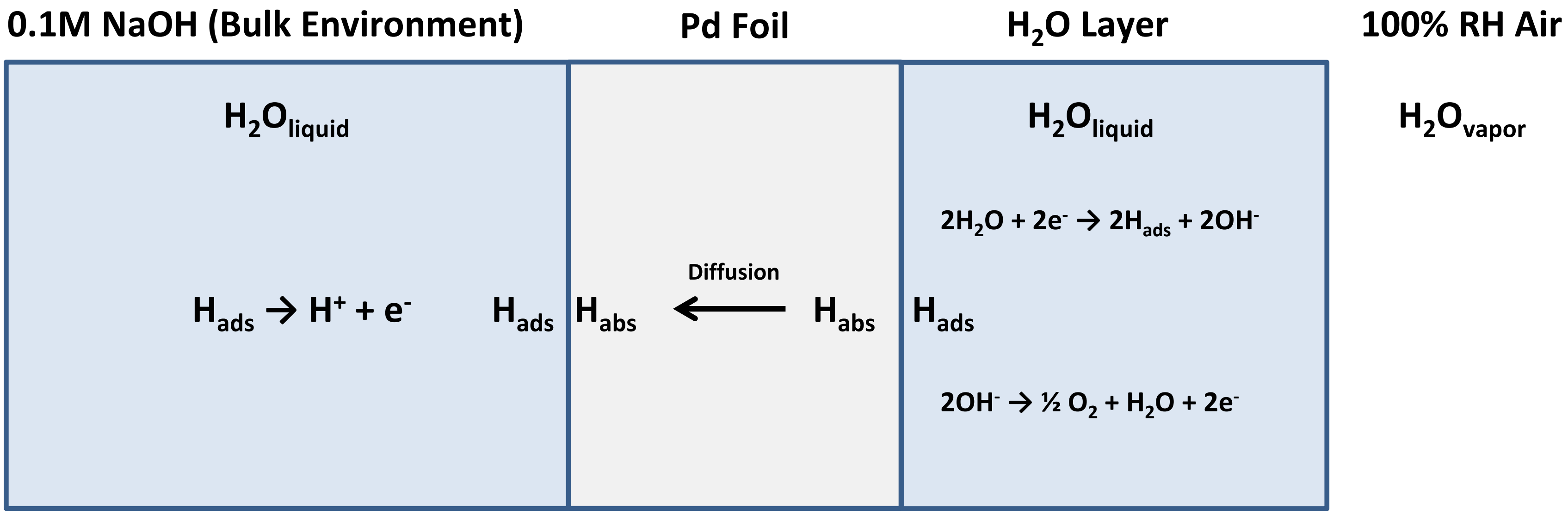
Figure 1 Experimental apparatus (schematic)

[1] Nitrogen gas flask.
[2] Water to moisten gas.
[3] Specimen flasks (3).
[4] Water bath
[5] Cold trap to remove excess water
[6] Gas chromatograph
[7] Gas flow rate meter

- Simpson and Schenk (1987) – attempt to directly measure hydrogen
- Synthetic granitic groundwater and a sodium chloride solution
- Detection limit of 3.7 x10^{-8} g(H_2)/h*m^2 (4000 times below Hultquist values)
- Also ran stagnant conditions, reducing detection limit by an additional factor of 10
- No hydrogen detected for replicate experiments performed at 50 and 80C

Could there be another source for the hydrogen observed by Hultquist?

- Bojinov (Corrosion Science 52 (2010) 2917–2927) demonstrated that hydrogen could be produced due to dissolution of the pre-existing Cu_2O layer (i.e., corrosion of the Cu not required)
- Hydrogen has only been observed when the Pd layer is present – perhaps it plays a role?



0.1M NaOH (Bulk Environment) | **Pd Foil** | **H_2O Layer** | **100% RH Air**

H_2O_{liquid}

$H_{ads} \rightarrow H^+ + e^-$

H_{ads} H_{abs} $\longleftarrow$ H_{abs} H_{ads}

Diffusion

H_2O_{liquid}

$2H_2O + 2e^- \rightarrow 2H_{ads} + 2OH^-$

$2OH^- \rightarrow ½ O_2 + H_2O + 2e^-$

H_2O_{vapor}

So what’s going on?

- Traditional thermodynamics indicate that Cu should be stable in anoxic water
- Attempts to replicate Hultquist’s results have been unsuccessful
- But – Hultquist has clearly observed attack of the copper accompanied by sustained hydrogen evolution – the question is, why?

Selected Modeling Results

- Belonoshki, 2010 (Langmuir vol. 26(21), pp. 16267-16270) – via molecular dynamics calculations, water may dissociate on Cu surfaces, and OH preferentially adsorb onto Cu (forming $CuOH_{ads}$) – but once formed, this would hinder further reaction unless some means to expose the Cu metal took place (e.g., nanoparticle formation?)

- Johansson, 2011 (The Journal of Chemical Physics, Vol. 135, 084709) – hydrogen gas may be evolved due to water cleaving/hydrogen recombination on the copper surface, which in turn results in the formation of a hydroxyl layer. The hydroxyl layer would then hinder further evolution.

- Werme, 2010 (Catal. Lett, Vol. 135, pp.165-166). Indicated that Hultquist's calculations stated that hydroxyl was the starting point, but used energies of a charge-neutral isolated OH molecule. When calculations were performed using the proper starting point, no copper oxyhydroxides or copper hydroxide species were found to be stable relative to Cu_2O.

- Taylor, 2008 (JECS Vol. 155(8), pp. C407-414) – the dissociation of water on Cu nanoparticles is enhanced, but the resulting modified Pourbaix diagram still places the water reduction line within the stability field for metallic copper.