ROYAL INSTITUTE OF TECHNOLOGY

**Scientific workshop on**

**Mechanisms of Copper Corrosion in Aqueous Environments**

**arranged by The Swedish National Council for Nuclear Waste (Kärnavfallsrådet)**

**16 November 2009**

# "Questions, hypotheses and facts related to corrosion of copper in water"

**Presented by Ass. Prof. Gunnar Hultquist**

# “Questions, hypotheses and facts related to corrosion of copper in water”

A global issue

What is the problem?

Results/facts

Suggestions

Summary and implications

# The safe storage of nuclear waste is a global issue

The Swedish method of copper containment was launched in early 1980 during political turmoil in Sweden and the model was **claimed to be based on proven science.** The method was also aimed to be used by other countries.

At that time a plan for final storage of spent nuclear fuel had to be presented before any new power plant could be commissioned. One million years of safe durability was originally required but today “only” 100 000 years is claimed with a thickness of 50 mm copper.

Even with this thickness a risk for local attack is considered in the Swedish method and the general corrosion attack is assumed to be zero when attacked by pure water.

# The Swedish model:

# KBS-3

- The concept was developed 30 years ago and consists of a copper canister surrounded by clay deposited 500 m down in the Swedish ground.
- The Swedish model, differs from other countries concept, since it assumes thermodynamic immunity in water, i.e. copper must withstand water also at elevated temperatures.
- This assumption of immunity is disputed.

# The main corrosion reactions that take place in the repository environment

1) Cu + $O_2$ (dissolved in ground water) $\Rightarrow$ Cu-oxide

When the oxygen is consumed:

2) Cu + sulphide ions in water $\Rightarrow$ Cu-sulphide

3) Cu + water molecules $\Rightarrow$ Cu-hydroxides +$H_2$+hydrogen in Cu-metal

There is a consensus regarding reaction 1 and 2. Reaction 3 is disputed and the source of today's discussion

# How is copper corroded by pure water?

$(H_2O \rightarrow OH^- + H^+) \Rightarrow CuOH + \mathbf{H_2}$ + hydrogen in Cu

where $\mathbf{H_2} \approx 10^{-3}$ bar at 20-80°C

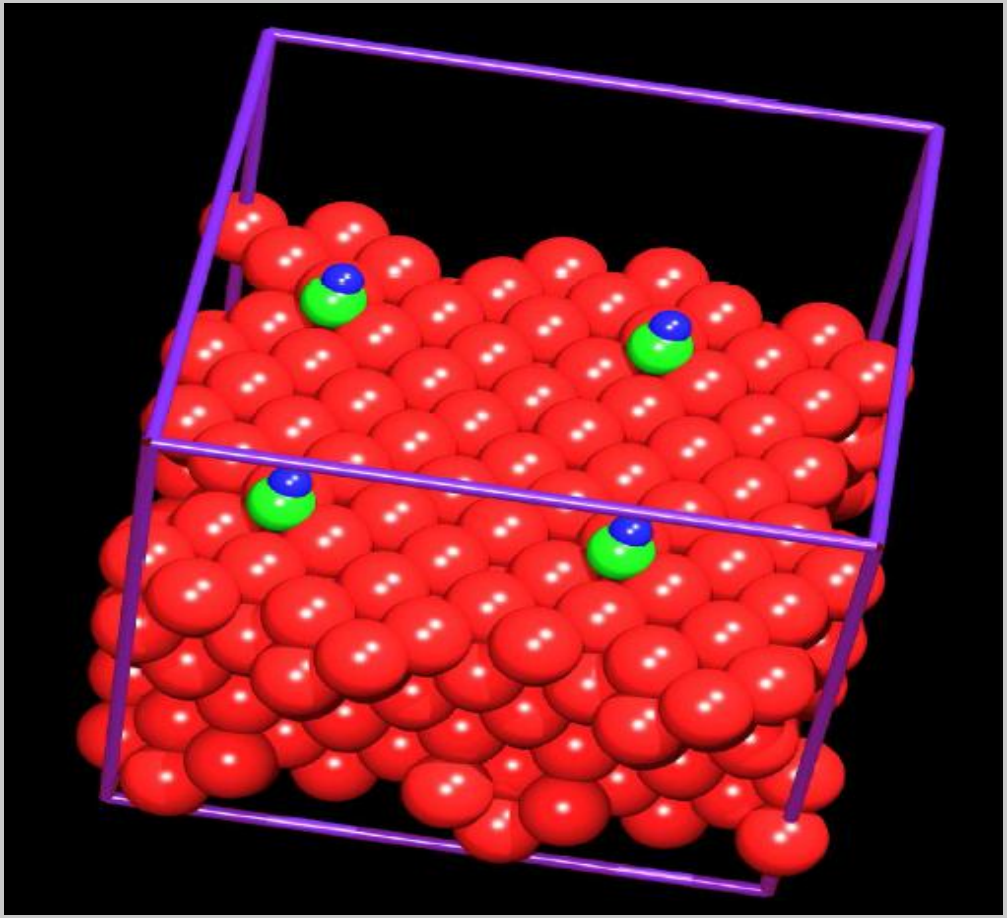
since **$H_2$-pressure** in air is $5 \cdot 10^{-7}$ bar it follows that

**copper is corroded by water**

In the Pourbaix diagram this “new” situation is shown by displacing the “hydrogen electrode” and thereby adjusting it to our present hydrogen content in air

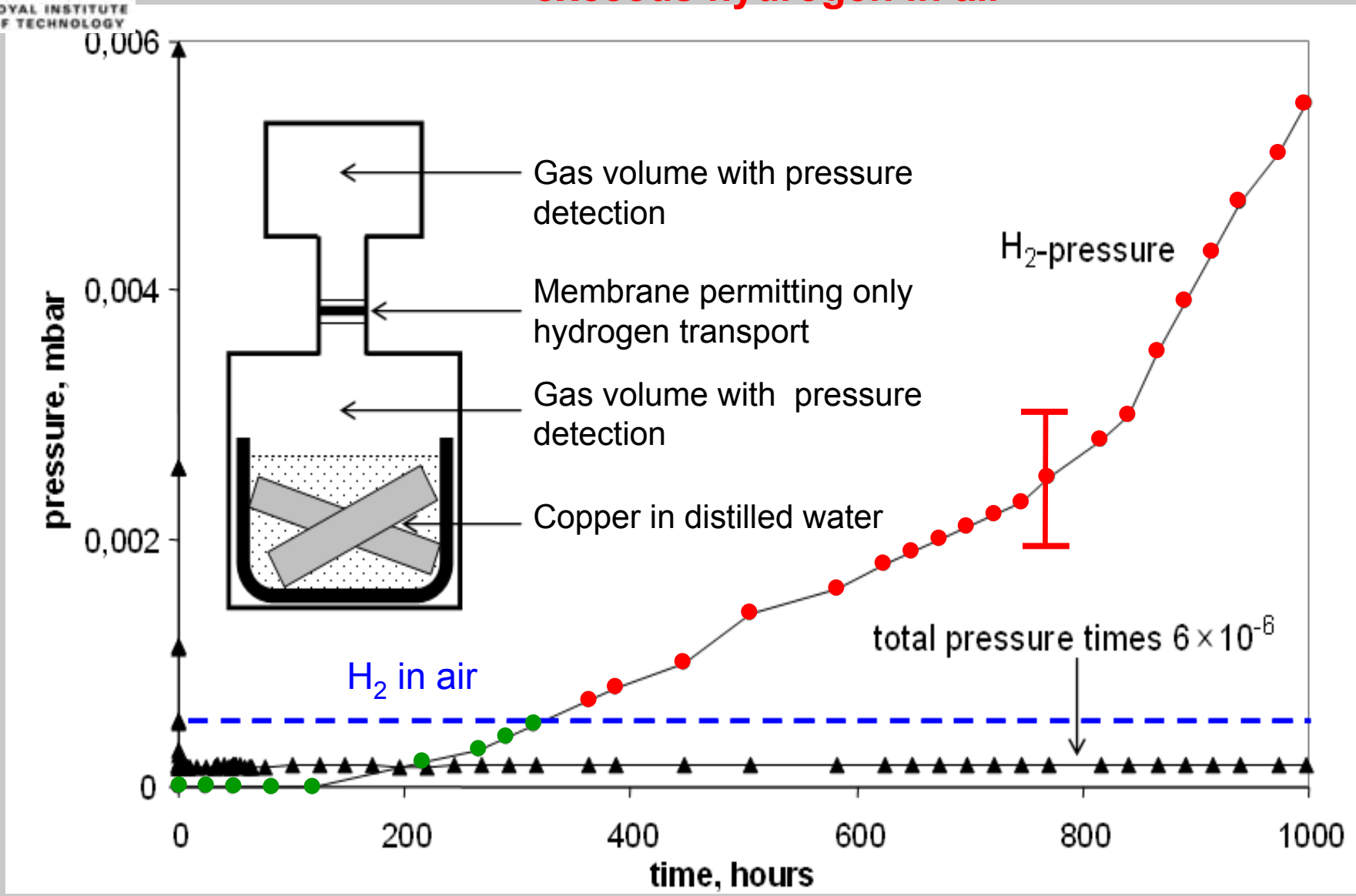
**In the peer-reviewed Journal Catalysis Letters, 2009**

First principles simulation of hydrogen (blue) and oxygen (green) with results of a strong bond of an OH-group to a Cu-(100) surface indicating growth of a 3-dimensional copper hydroxide

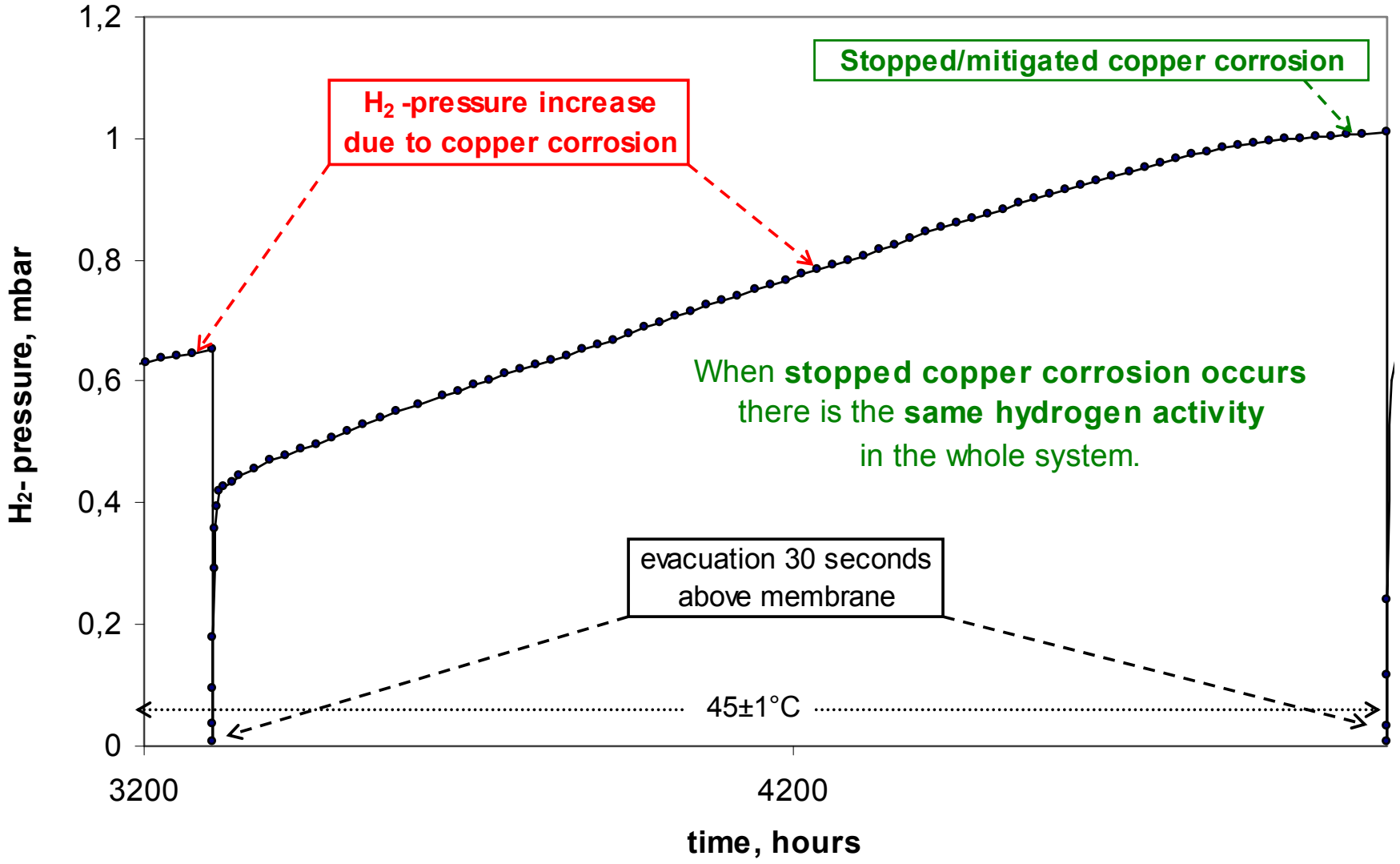


In the peer-reviewed Journal Catalysis Letters, 2009

# Hydrogen from copper corrosion at room-temperature exceeds hydrogen in air



# The hydrogen pressure reaches $10^{-3}$ bar due to copper corrosion and is temperature dependent



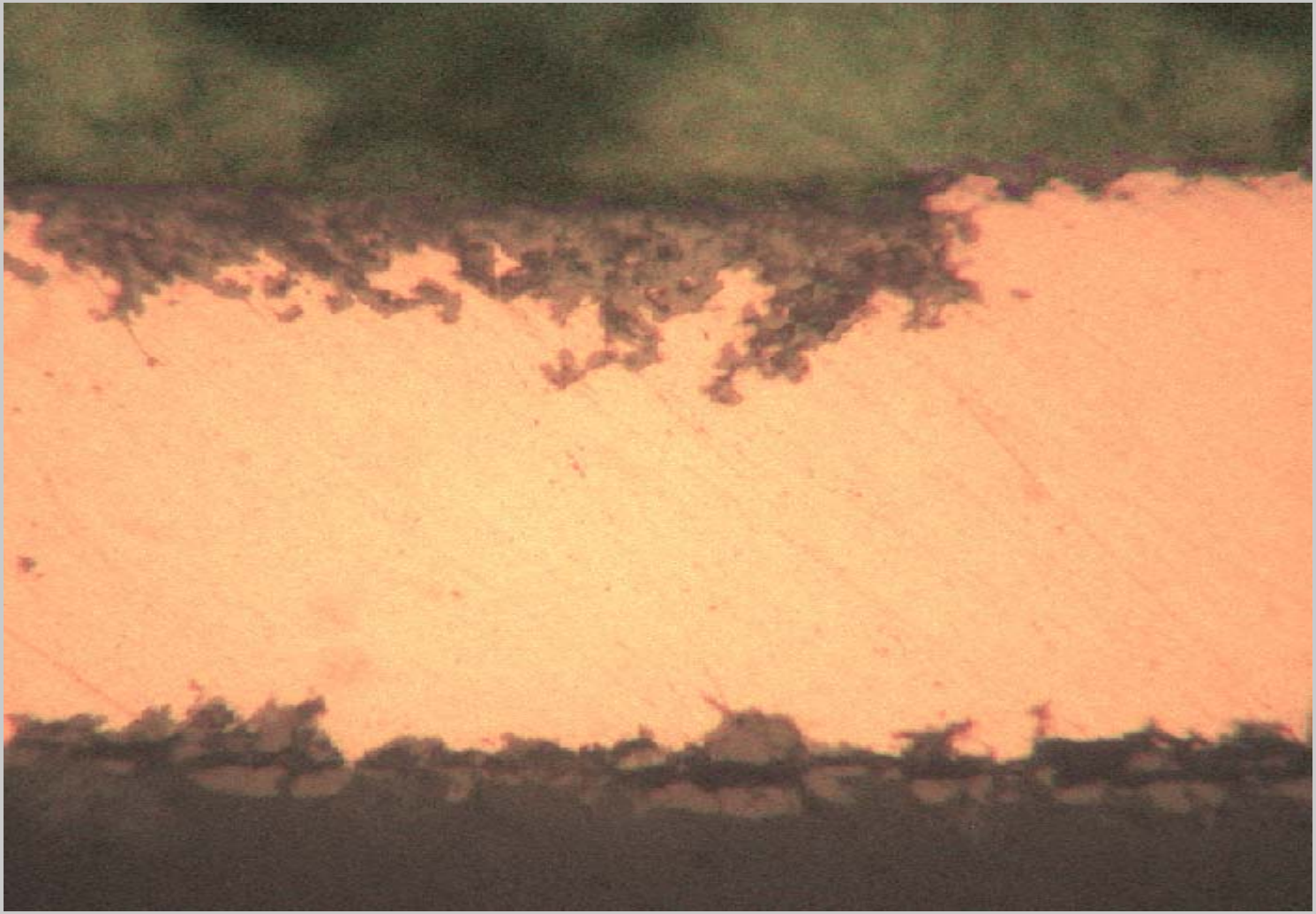
# Copper in water after 15 years at room-temperature

Copper corrosion without access to $O_2$ and no removal of $H_2$


Copper corrosion without access to $O_2$ but with removal of $H_2$

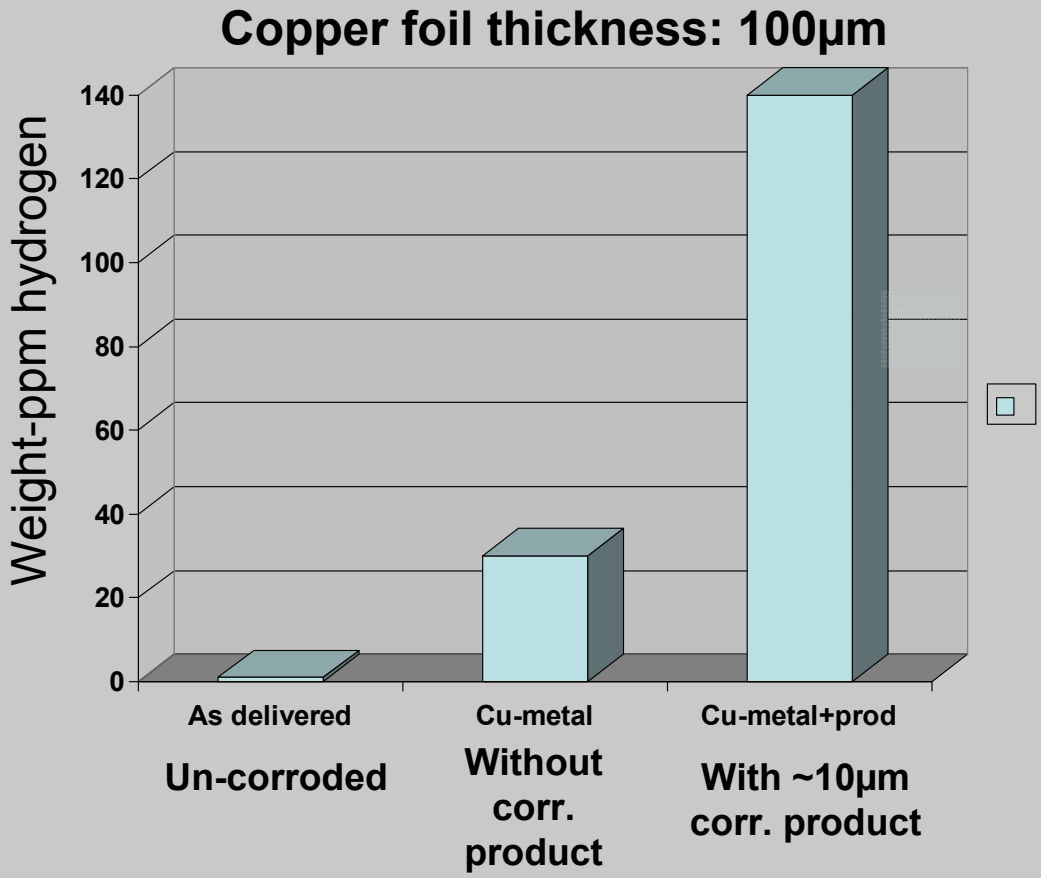
# Cross section of 0.1 mm copper foil after 15 years of water exposure at room-temperature

Various kinds of corrosion



# 15 years exposure of corroded copper in distilled water

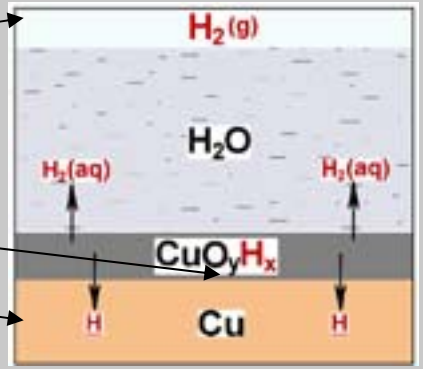
Integrated removal of hydrogen from reaction product and underlying “metal” by outgassing in vacuum at 20-700 °C. Also unexposed copper is taken as a reference.

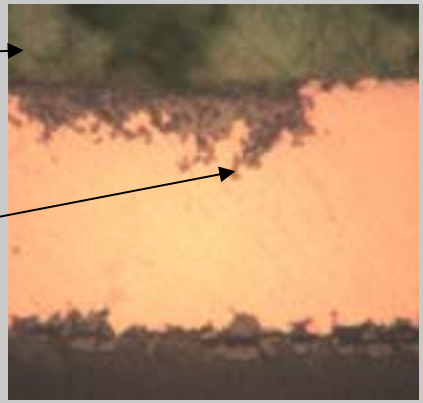



Hydrogen detected both in secondary ion mass spectrometry and in quantitative out-gassing in vacuum.

# Evidence of Cu corrosion by water has been verified through the following research results

- Formation of hydrogen
- Increase of weight
- Hydrogen in the Cu metal
- Chemical analysis of the corrosion product
- Visual inspection
- Metallographic examination

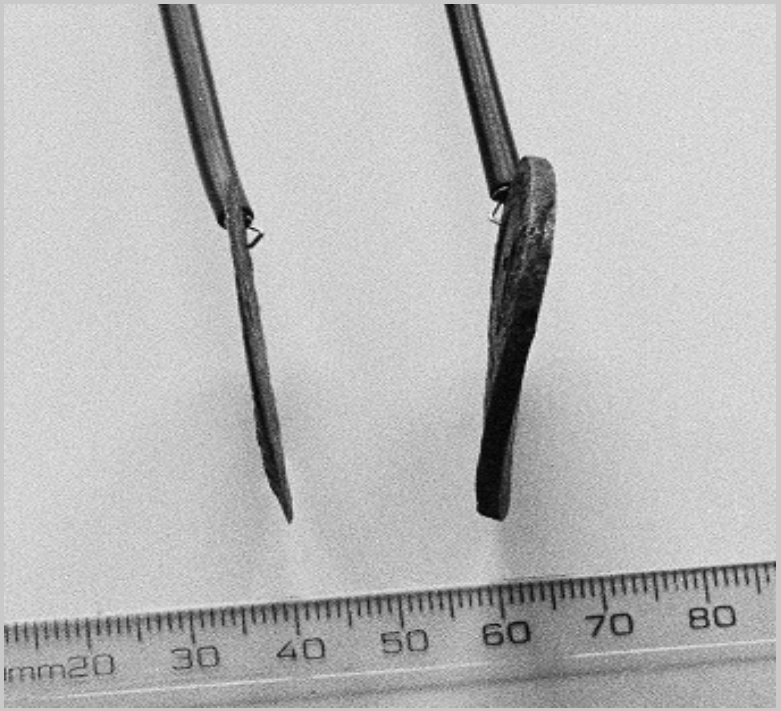


# 331 years exposure of 1 öre copper coins from War Ship Wasa

Photo of the coins published already in **1984** in Dagens Industri with text saying that we can naturally not know exactly the water chemistry during this exposure

Photo of the coins also published **2009** in Catalysis Letters with data connected with a hatched line to corrosion data from exposure in distilled water at room-temperature

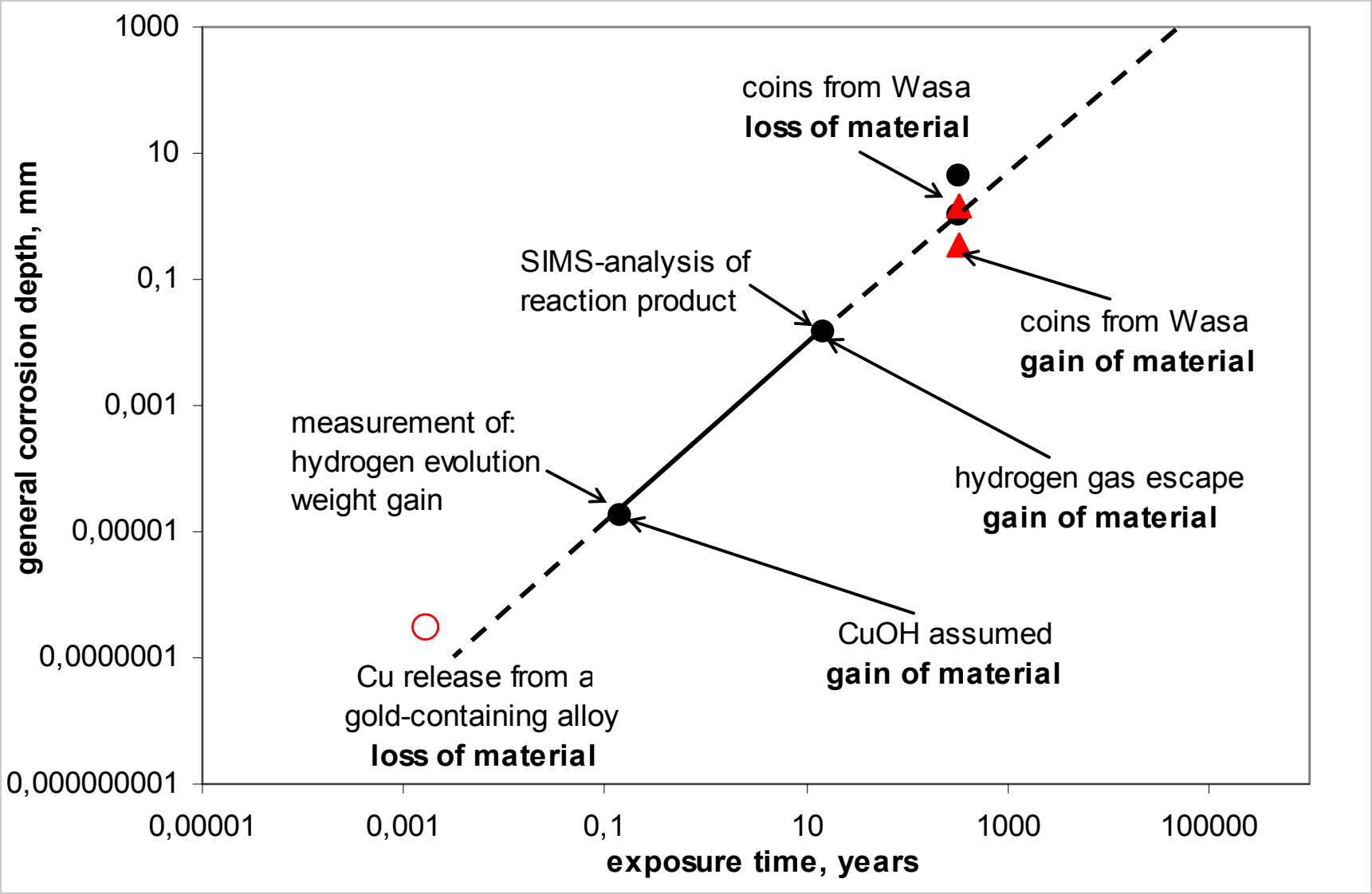



**One hypothesis which is consistent with all other experimental observations:**

**Copper corrodes by water itself and therefore copper corrosion takes place regardless of molecular oxygen.**

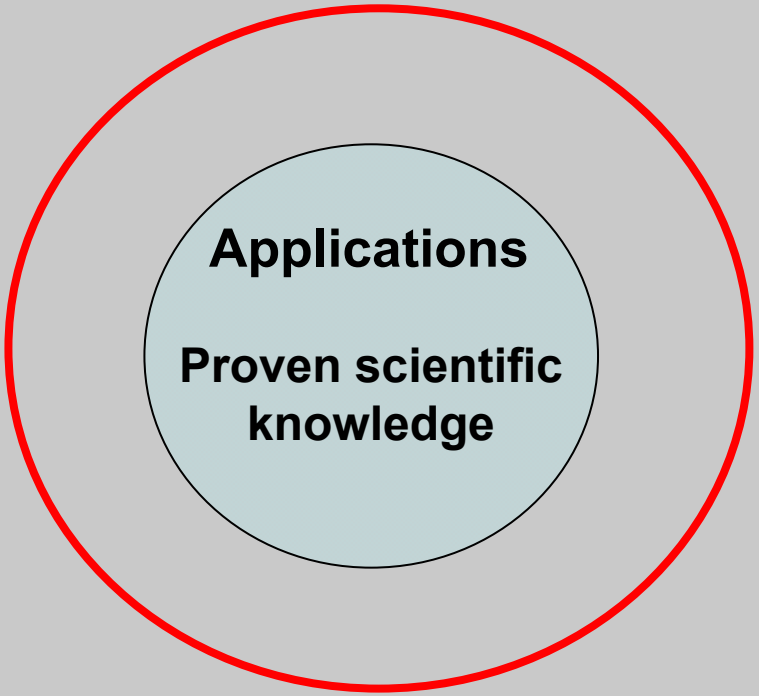
In the peer-reviewed journal Catalysis Letters, 2009

# What is expected for copper in long time water exposure?



# A Swedish model for long time storage of nuclear waste must be based on proven scientific knowledge

The present Swedish model is not proven by scientific knowledge



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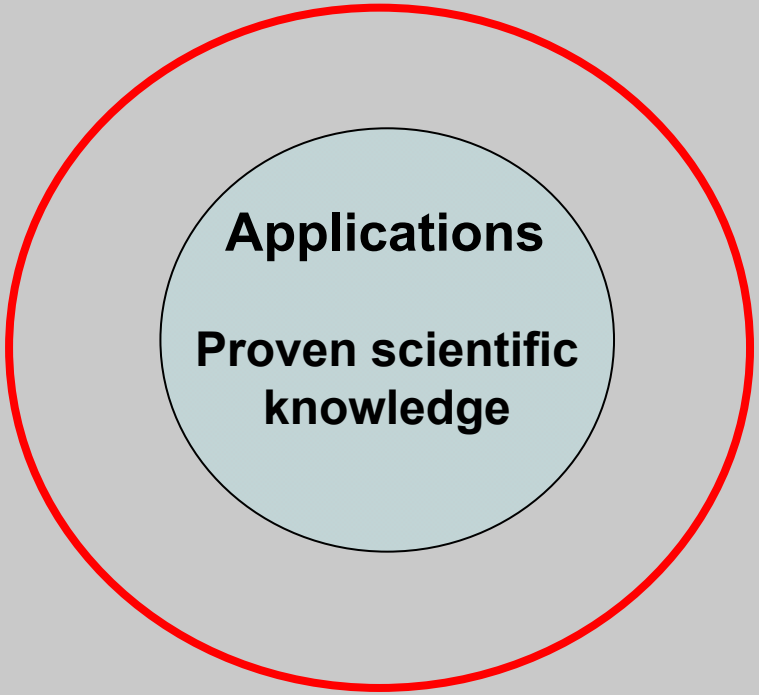
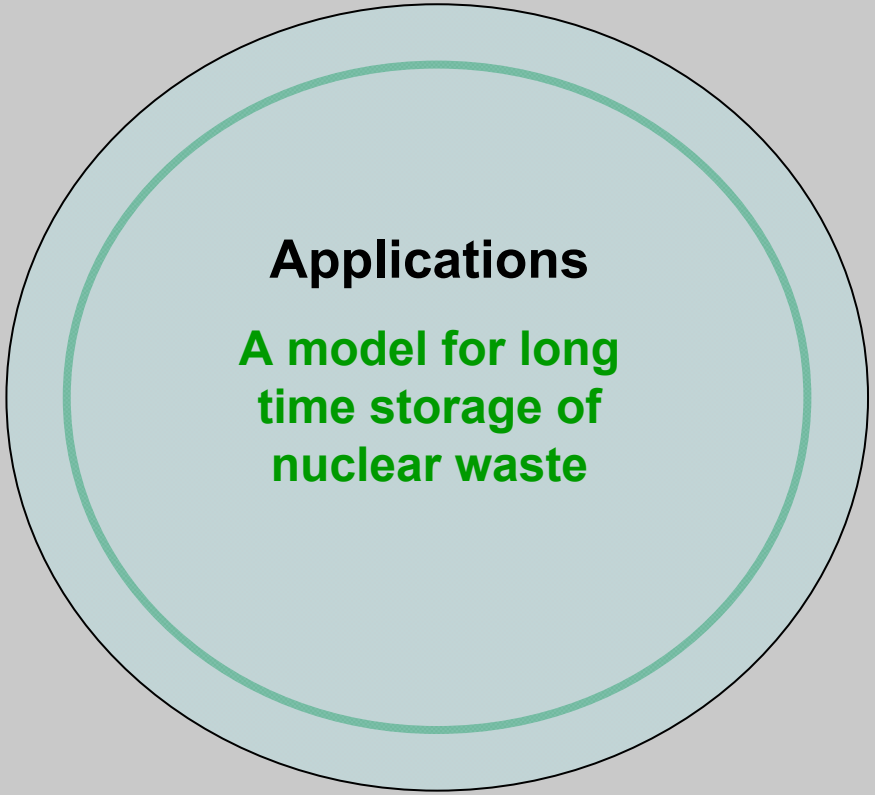



A Swedish model



## Suggestions for controlled studies of water reactions at ~50°C with the aim to make the "Swedish model" more scientific

1. Oxidation by distilled water is studied by measurements of hydrogen evolution and hydrogen uptake in various metals and high alloyed stainless steels.

2. Copper and the materials in 1. are studied in ground water

3. Predictions are made based on simulations/theories that are independent, yet consistent, with experimental findings

# Summary and implications

- All observations, both experimental and theoretical, during 25 years, are consistent with the fact that water corrodes copper.

- These observations can have an influence on the present Swedish method for storage of spent nuclear fuel, KBS-3.

- To make the Swedish model KBS-3 more scientific, hydrogen release in metal corrosion must be monitored with results published in peer-reviewed journals.