

Workshop on "Mechanisms of Copper Corrosion in Aqueous Environments" 16th of November 2009

Thermodynamics and kinetics of copper corrosion in oxygen free water

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Background

It was known already 30 years ago that copper was not thermodynamically immune in pure O₂-free water (**Undisputed among thermodynamic experts**)

Our research results does not change the known thermodynamics regarding water corrosion of copper. The results can be explained by assuming the formation of an amorphous copper hydroxide.

Several scientific publications suggest the existence of different amorphous copper hydroxides, both monovalent and bivalent ¹⁻³, which easily converts to oxides, especially upon exposure to air ¹.

- 1) C. H. Pyun and S-M Park, J. Electrochem. Soc. 133, (10) p. 2024 (1986)
- 2) J. Kunze et al., Corr. Sci. 46, p. 245 (2004)
- 3) J. Kunze et al., J. Electroanalytical Chem. 554-555, p. 113 (2003)



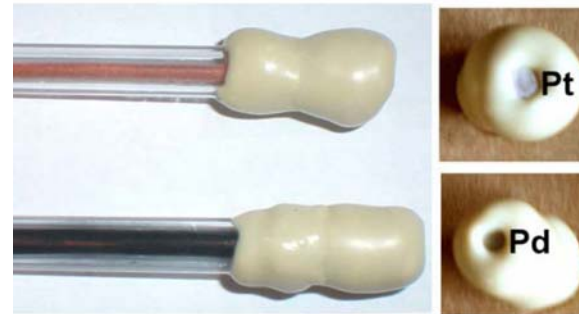
SKB has referred to four papers during 23 years which are claimed to support the assumption of zero copper corrosion in O₂-free water.

- **Two papers in *Corrosion Science*, 1987 and 1989 which we disregard since O₂ were present in the experimental set-up.**
- **Two papers in *Mat. Res. Soc. Symp. Proc.* (MRS), 2004, which were based on an “On-line Copper Corrosion Probe”. The reliability of this probe in complex environments is seriously questioned.**

These four papers with our comments are submitted to the Expert Panel, see www.karnavfallsradet.se

Only one study (attempt) has been performed during the latest 23 years to repeat Hultquists experiment: SKI 95-72 ⁴

In this study, only one experiment was performed according to Hultquist's instructions.



That specific experiment did indeed indicate that copper corrodes in O₂-free water.

However, no follow-up was ever done.

4 Conducted at Swedish National Testing and Research Institute (SP) in Borås 1995. The report is in Swedish.

“Natural analogues” Native metals



Native copper from Keweenaw
Peninsula, Michigan, USA.
(SSM-report 2009:28)



Native iron from Ovifak on Disko island,
Greenland (22 ton boulder). Found by the
explorer A. E. Nordenskiöld 1870. (The
Swedish Museum of Natural History)

It has been claimed that copper canisters should be corrosion resistant since native copper is found at some few locations in the world. However, the situation is the same for native iron (and nickel, zinc etc) but no one is using this argument to state that iron should be corrosion resistant in groundwater! (Groundwater contains chlorides, sulphides, sulphates and methane/acetate etc)

“Archaeological analogues”

Bronze cannons from the warship *Kronan*, wrecked 1678

**Quotation from Sv. D.,
Vetenskap, 31 Aug. 1986:**

– Kanonen utgör ett unikt prov på vad som långsiktigt händer med koppar under förhållanden som förbluffande mycket påminner om dem som kärnbränslekapslarna kommer att utsättas för.

...an environment that is astonishingly similar to that the copper canisters will be exposed to.

(The sediment of the Baltic Sea with clay and O₂-free brackish water)



En av regalskeppet Kronans kanoner omedelbart efter bärgningen.

The corrosion of bronzes differs fundamentally from that of copper. An enrichment of passivating tin forms on the bronze surface that strongly reduces the corrosion rate in aqueous environments, this was known already 30 years ago.

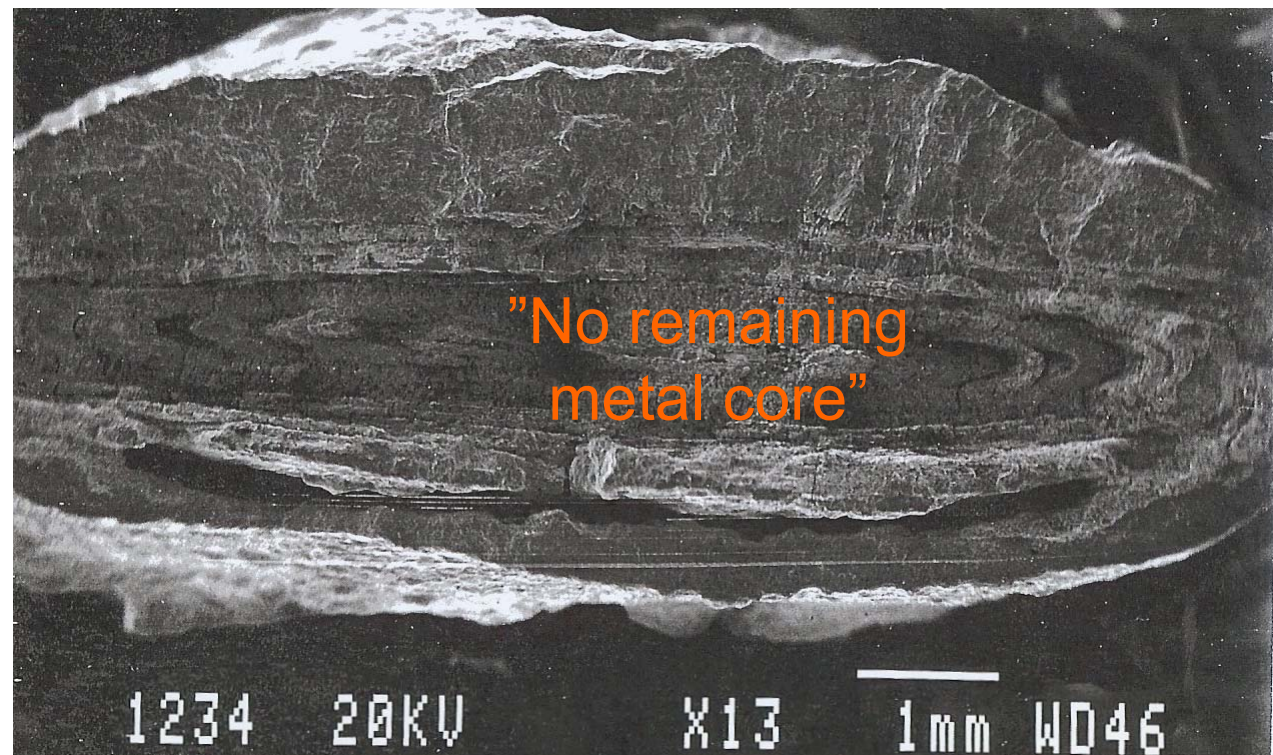
Archaeological analogues: Marine Copper Finds

Studies in Conservation 38 (1993) 133–135

A NOTE ON SPIONKOPITE AS A CORROSION PRODUCT ON A
MARINE COPPER FIND

Anders G. Nord, Karin Lindahl and Kate Tronner

Copper coins on
Kronan were more
corroded than on
Wasa and several
Kronan-coins had
no remaining
metal core left



Fracture surface of a copper compass ring from the warship *Kronan*, wrecked in the Baltic sea 1676. 100% copper sulphide.

Olof Arrhenius

Corrosion on the Warship Wasa

Corrosion Bulletin 48 (1965)

Corrosion on the Warship Wasa

U = Upper gun deck

L = lower gun deck

O = orlop deck

H = hold



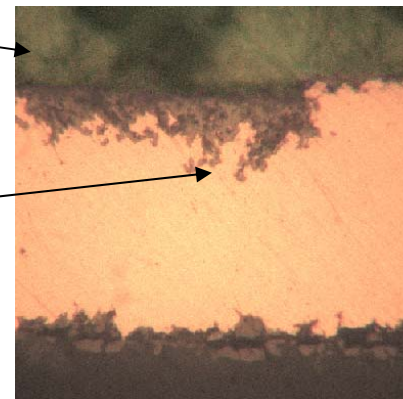
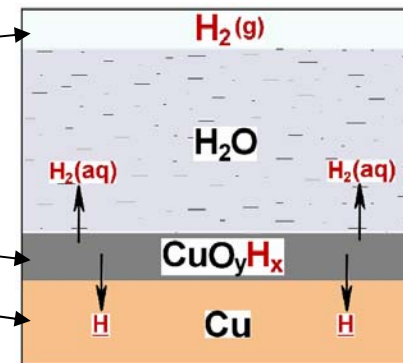
Copper objects	U	L	O	H	Total
Copper plate	10	10	1	7	28
Coin, round	754	272	117	427	1570
„ square	1039	60	71	675	1845

The corrosion rate of the 1 öre copper coins from 1627-28 was in the $\mu\text{m}/\text{year}$ range, same rate as Hultquist et al. reported independently in 1985/ 2009.

Our corrosion results

The presence of copper corrosion on pure O₂-free water have been verified by following observations:

- H₂-gas detection
- Weight gain
- H-uptake in copper metal
- Chemical analysis of the corrosion product
- Visual inspection
- Metallographic examination



STATOR COOLING WATER

Corrosion in the stator cooling system of power generators is a primary source of maintenance costs and plant downtime.

Copper corrosion in O₂-free water is a well known industrial problem.

All copper cooling system for power generators and accelerators (CERN etc) corrodes (0.5-10µm/y)

Environment: Deionised and degassed water around 70°C



Study identifies copper corrosion problems with water-cooled generators, EPRI

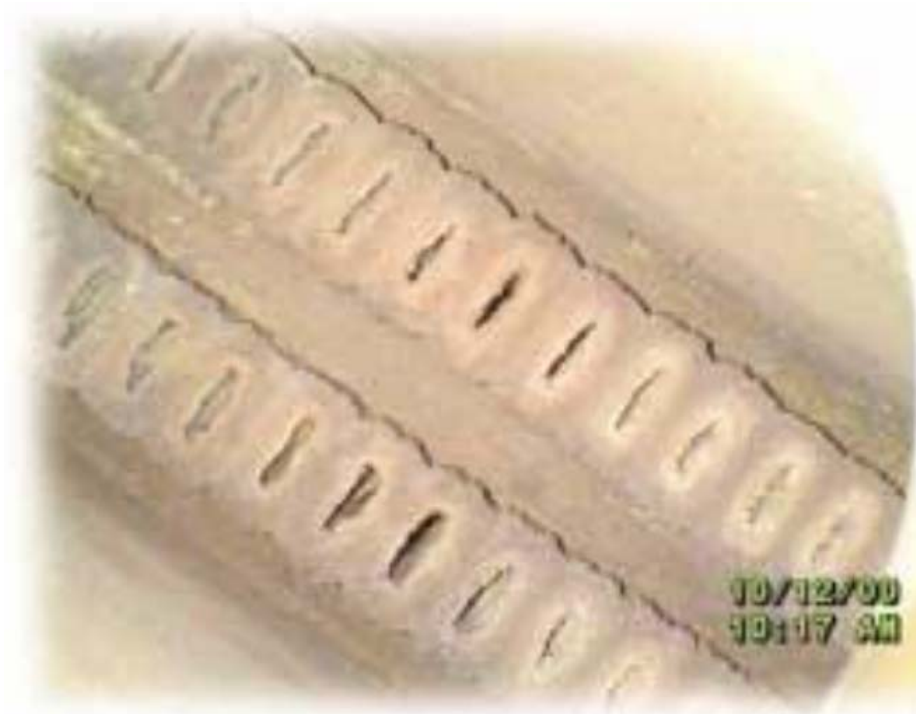


Figure 1. Partial plugging by copper corrosion products (oxides and hydroxides) prior to cleaning of water-cooled generator at SONGS 2. Photo courtesy of EPRI

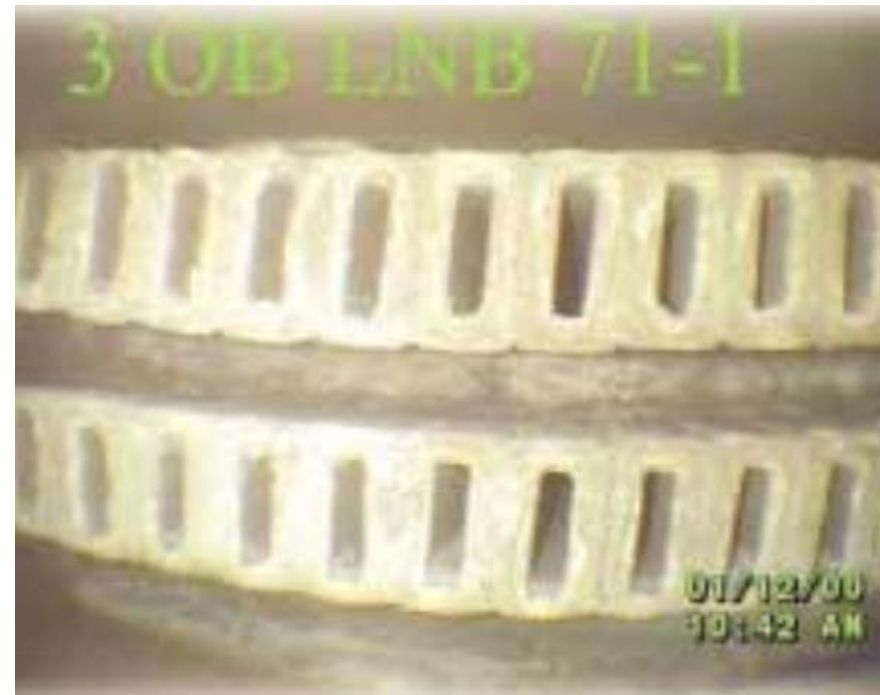
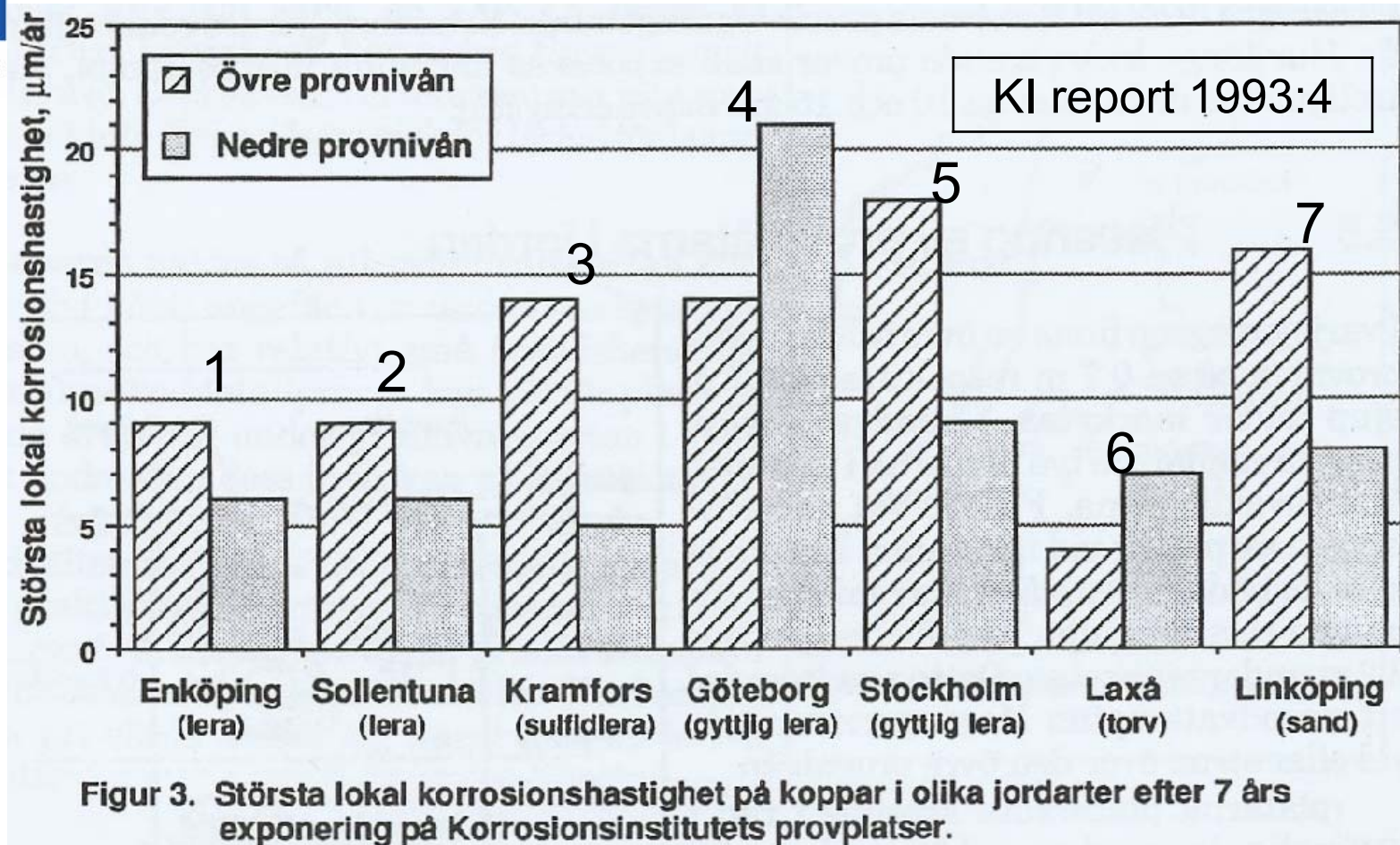


Figure 2. Videoscopic inspection after Cuproplex cleaning of SONGS 3 water-cooled generator. Photo courtesy of EPRI

Copper corrosion rates in Swedish clay and soils



Low redoxpotentials were recorded in test sites 2, 3, 4 and 5, which indicate O_2 - free corrosion.

Copper corrosion in repository environment

Ref. SKB report TR-01-23

Table 9-1. Comparison of predictions of long-term corrosion behaviour and canister lifetimes.

Country	General Corrosion	Localized Corrosion
Sweden/ Finland ¹⁾	0.33 mm in 10^6 yrs	0.33 mm in 10^6 yrs (realistic) 1.3 mm in 10^6 yrs (conservative)
Japan	9–13 mm in 10^3 yrs, depending on repository design	18–26 mm in 10^3 yrs based on pitting factor of 3, 2 mm in 10^3 yrs based on extreme-value analysis

Astonishingly low corrosion rate in Sweden: 0.33 nm/year, i.e. ~30.000- 60.000 times lower corrosion rate than in Japanese ground water.

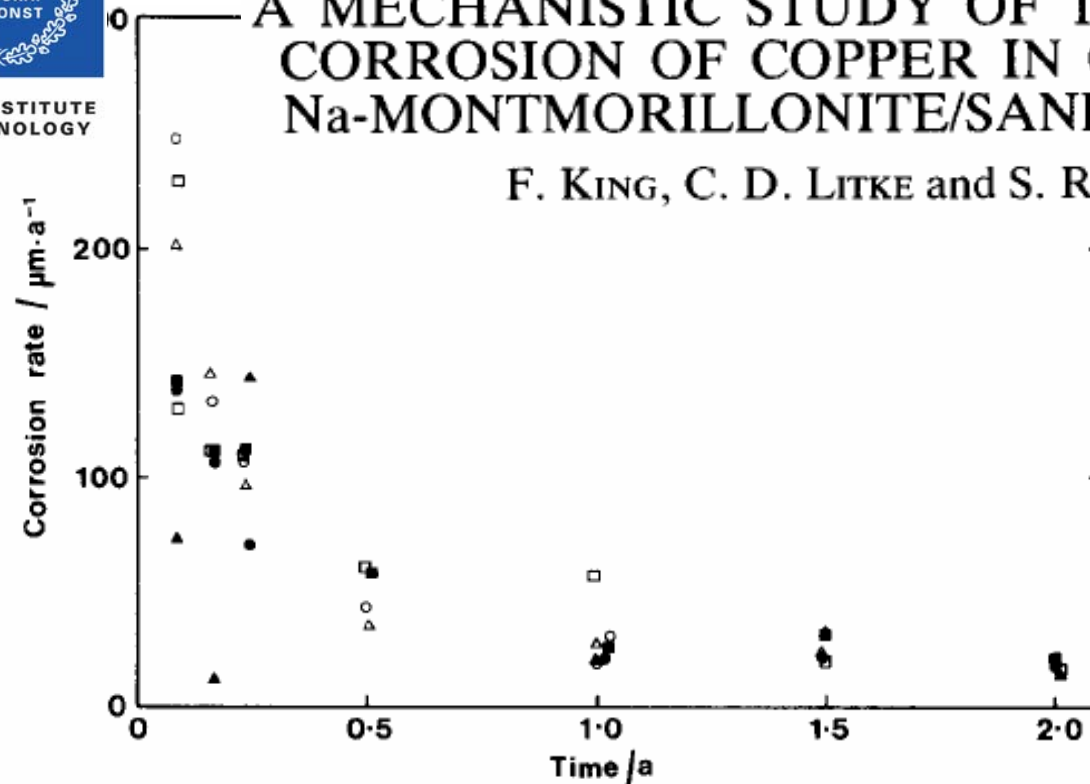
Example of measured corrosion rates

- Our research (RT): 0.5-5 $\mu\text{m}/\text{y}$
- Rosborg, LOT (30°C) : 0.5-3 $\mu\text{m}/\text{y}$ (bentonite)
- SKB, LOT-proj., (around 100°C) : 10-20 $\mu\text{m}/\text{y}$ (bentonite)
- Canada, F. King (50-100°C) : 15-20 $\mu\text{m}/\text{y}$ (bentonite)
- Finland, Posiva (80°C): 7 $\mu\text{m}/\text{y}$
- Swedish groundwater / clay and soil: 3.9-21 $\mu\text{m}/\text{y}$
- Japanese repository: 10-30 $\mu\text{m}/\text{y}$

SKB safety analysis: 0.003 $\mu\text{m}/\text{y}$, i.e. 1.000- 10.000 times lower than the measured corrosion rates.

A MECHANISTIC STUDY OF THE UNIFORM CORROSION OF COPPER IN COMPACTED Na-MONTMORILLONITE/SAND MIXTURES

F. KING, C. D. LITKE and S. R. RYAN



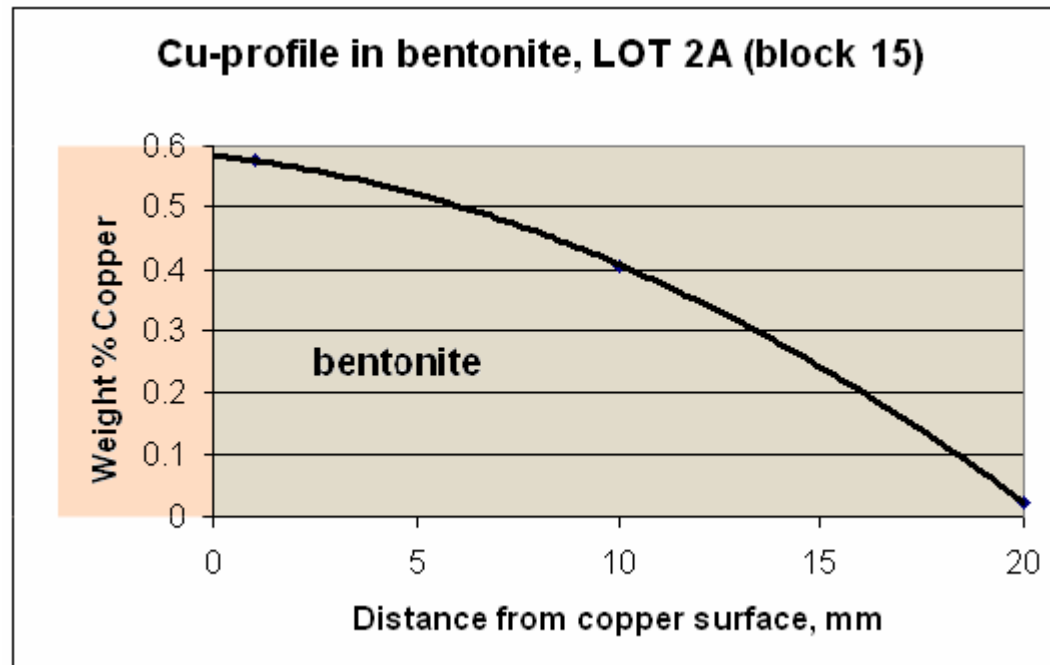
This laboratory study confirm the LOT *in-situ* exposure, i.e. the general corrosion rate of heated copper is 10-20 µm/y. It takes place with a dissolution-precipitation process in contact with bentonite clay/ ground water

FIG. 8. Copper corrosion rates determined from weight loss of coupon in contact with compacted buffer material in absence of γ -radiation. ● 50°C, 1.45 g cm⁻³ buffer density; ■ 50°C, 1.65 g cm⁻³; ▲ 50°C, 1.79 g cm⁻³; ○ 100°C, 1.45 g cm⁻³; □ 100°C, 1.65 g cm⁻³; △ 100°C, 1.79 g cm⁻³.

On page 1991, it was concluded that “O₂-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”.

LOT A2, Appendix 6:
**Mineralogical and geochemical alteration of the MX80 bentonite
from the LOT experiment –Characterization of the A2 parcel**
Bundesanstalt für Geowissenschaften und Rohstoffe

Data taken
from Table 2:



Heated copper
exposed for 5
years in the Äspö
laboratory

A significant part of the copper in bentonite are **precipitated as Cu- and Cu(Fe)-sulphides**, representing ca 4 $\mu\text{m/y}$ in corrosion rate. Considering the total amount of copper in corrosion product, bentonite and groundwater it is most likely that the copper corrosion rate is **at least 10 $\mu\text{m/y}$** (pitting corrosion not taken into account).

Microbially accelerated corrosion

(MICROBE laboratory in Äspö)

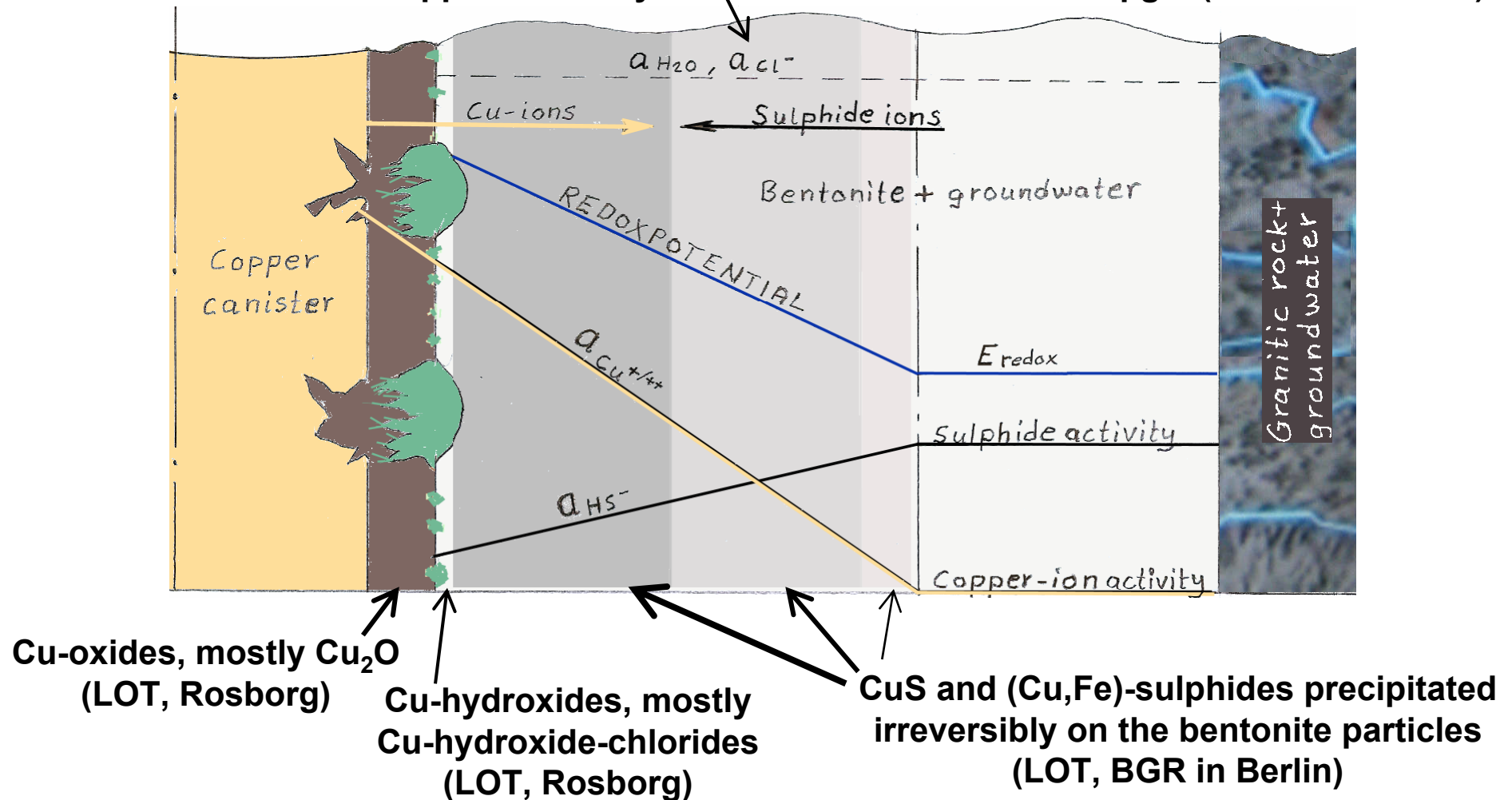
Bacterial activity in the repository environment produces both sulphide (from sulphate) and acetate (from CO_2 , H_2), thus affecting the chemistry, redoxpotential and copper corrosion.

"The sulphide and acetate production rate were determined to be 0.08 and 0.14 mg/L, respectively" ⁵

- Acetate and sulphide causes stress corrosion cracking (SCC) in copper, especially in phosphorus alloyed copper. (Details follow later)
- Copper metal/ions as well as Fe-ions act as a sulphide sink by precipitation of $(\text{Cu,Fe})\text{S}$, thus driving the microbial production of sulphide.
- The copper corrosion are consequently accelerated with precipitation of Cu-sulphides and (Cu,Fe) -sulphides in the bentonite (Confirmed by SKB's LOT-project).

A corrosion model explaining the observations from the LOT-project; copper exposed in ground water saturated bentonite

Copper solubility in saline water at 80°C: 2300µg/L (POSIVA 2003:45)



Intergranular corrosion (IGC) of copper

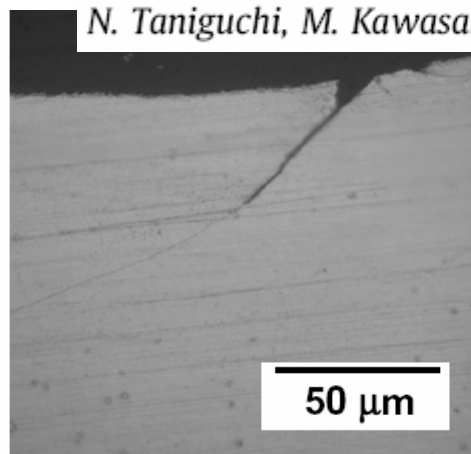
Electrochemical and Solid-State Letters, 11 (4) G15-G18 (2008)
1099-0062/2008/11(4)/G15/4/\$23.00 © The Electrochemical Society

Rapid Intergranular Corrosion of Copper in Sulfide-Polluted Salt Water

F. M. Al Kharafi, I. M. Ghayad, and B. G. Ateya^{*,z}

“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”

**The Forsmark
situation with
initially
dissolved O₂**



0.001M-Na₂S

Slow Strain Rate Testing, SSRT:
Synthetic seawater 80°C without O₂
Extension rate: 8.3E-7 s⁻¹

**Both Forsmark
and Olkiluoto,
groundwater
without O₂**

Stress Corrosion Cracking, SCC

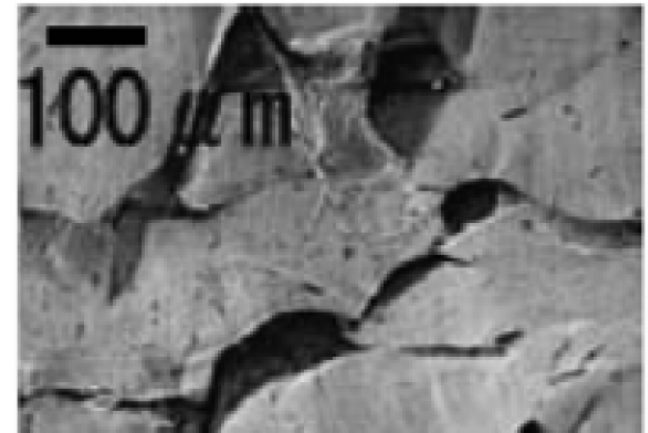
European Commission: 5th EURATOM FRAMEWORK PROGRAMME 1998-2002, COBECOMA, final report (2003). B. Kursten, L. Werme et al. Page 166:

”The candidate container material copper, and especially those containing phosphorus, has been found, in the past, to be highly susceptible to SCC”

N. Taniguchi and M. Kawasaki, Journal of Nuclear Materials 379, p. 154 (2008):

Sulphide, does indeed induce SCC in copper. “The threshold of sulphide concentration for the SCC initiation is likely to be in the range 0.005-0.01 M”.

The “**Forsmark situation**” with hot copper and groundwater evaporation \Rightarrow salt/sulphide enrichment:

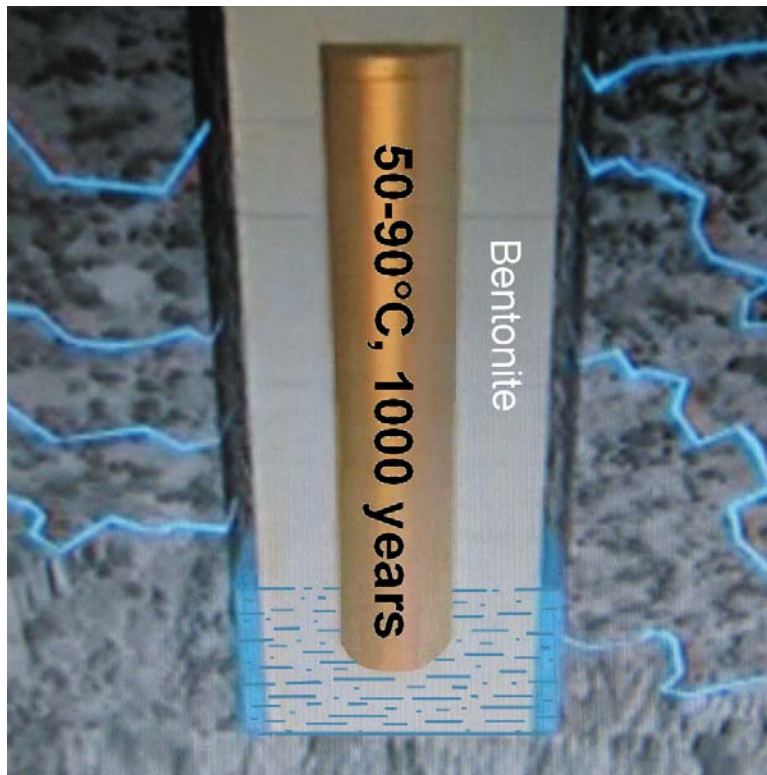


SCC at 80°C on OFHC-Copper with 45ppm P

SCC is likely to occur within the first 1000 years

Conclusions regarding the “Forsmark situation” :

It could take up to 1000 years to fully water saturate the bentonite
(According to SKB 2009)



- Atmospheric corrosion: up to **0.3 mm/year** at 90°C (E. Mattsson)
- Moist gas phase corrosion with salt: $\mu\text{m}/\text{year}$?
- Evaporation induced salt/sulphide corrosion, Several **$\mu\text{m}/\text{year}$ - mm/year** (IGC, SCC)
- Groundwater and bentonite induced general corrosion, up to **20 $\mu\text{m}/\text{year}$** .
- Hydrogen embrittlement.

Conclusions

Corrosion of copper by oxygen-free water is a well-known mechanism in industrial copper-cooling systems and synchrotrons.

It has been found experimentally that the corrosion rate of copper by water is in the order of 1-30 $\mu\text{m}/\text{year}$ depending on the temperature.

The corrosion rate of copper in wet bentonite or soil has been found to be 1-30 $\mu\text{m}/\text{year}$. This corrosion rate of copper is 1 000 to 10 000 higher than SKB's theoretical assumption.

The copper canister will have an elevated temperature of 40-100°C during the first 1 000 – 2 000 years in the repository. The situation at the planned repository at Forsmark is during this period complex and most severe from both corrosion and embrittlement point of view.

The copper canisters will be exposed initially for some years to atmospheric corrosion before the oxygen is consumed.

Conclusions cont.

The copper canisters will independent of the oxygen content be subjected to water corrosion, sulphide corrosion, salt corrosion, stress corrosion cracking, intergranular corrosion, evaporation induced corrosion (deliquescent salts corrosion) and dissolution-precipitation corrosion.

The KBS-3 concept must be experimentally verified under the conditions prevailing at the Forsmark repository. Due considerations must be taken to the corrosion mechanisms including hydrogen embrittlement and their effect on the mechanical properties of the copper canisters.

A recommendation was formulated in the SKI report 96:38 regarding a verification of the KBS-3 model. “Copper of identical composition as the future canisters, should be placed in a future site environment, i.e. artificial heating at about 80°C, a bentonite surrounding etc. Such an experiment could be monitored for several decades. Even 10-30 years is a short period of time in the present context.”

Copper canisters stored 18 years in a moist cellar



Prize awarded photographs by David Masel (Sv.D. 2009)