

**Från:** Johan Swahn johan.swahn@mkg.se   
**Ämne:** Re: Skrivelse till SSM angående LOT (SSM 2020/5740)  
**Datum:** 3 november 2020 14:50  
**Till:** Bo Strömberg Bo.Stromberg@ssm.se  
**Kopia:** Michael Egan Michael.Egan@ssm.se, Ansi Gerhardsson ansi.gerhardsson@ssm.se, Henrik Öberg henrik.oberg@ssm.se, Christine Anvegård christine.anvegard@mkg.se, Joachim Stormvall joachim.stormvall@mkg.se, Oscar Alarik oscar@alarik.se, Strålsäkerhetsmyndigheten registrator@ssm.se

Hej Bo!

Tack för dina frågor. Har har du MKG:s svar.

#### Punkt 4 om oxic vs anoxic

Det är helt riktigt att det ska stå "oxic" i stället för "anoxic" på de två ställen du uppmärksammar i skrivelsen. Jag bifogar en rättad version som ska ersätta den tidigare skrivelsen.

Rörande korrosionsprodukter vid oxisk eller anoxisk korrosion har jag förstått att om den anoxiska korrosionen kommer från syre i vattenmolekyler blir korrosionsprodukterna samma som vid oxisk korrosion. Möjligtvis blir det dessutom mer förklarligt att det finns korrosionsprodukter med hydroxid i om anoxisk korrosion där vattenmolekyler är inblandad förekommer.

#### Punkt 2 om FEBEX-resultaten

Rörande korrosionsdjup i FEBEX gäller 100 µm specifikt det djup som finns i bilden på sidan B-5 i Nagra-rapporten NAB 16-16 som finns som appendix 1 till skrivelsen. I texten som beskriver bilderna står det:

"The maximum penetration depth for this zone is about 100 microns. Apart from this, the copper coupon shows a generalized corrosion."

Författaren pratar om "localized corrosion". Det är något osäkert vad författaren menar med "zone". Det ser ju ut som om det finns begynnande gropar runt om kopparkupongen även om det främst är gropar på den sida där förstöringen finns.

#### Punkt 3 om LOT A2

Rörande hur mycket koppar som kan finnas kvar i korrosionsprodukter på en yta där lera avlägsnats hävvisar jag till sidan 4 i appendix 11 till skrivelsen med benämningen "Correspondence between Peter Szakálos KTH and Stephan Kaufhold BGR 090602-090603". Jag inser att korrespondensen påbörjades redan den 28 maj och inte den 2 juni, men där skriver Peter Szakálos:

"My estimation was based on copper profile data from copper/bentonite exposures in Canada (F. King et al.) where he correlated the profiles with actual weight loss measurement. Roughly, if I remember correct, by multiplying the corrosion rate based on "Cu-profile in bentonite" with around 5 it gave the "true" total corrosion rate."

Jag har grävt vidare i frågan och utgående från sidan 15 i Peter Szakálos presentation på Kärnavfallsrådets möte om kopparkorrosion den 16 november 2009 som bifogas har jag identifierat källan "F. King et al." (1). Jag förstått att referenserna är den bifogade artikeln "A Mechanistic Study of the Uniform Corrosion of Copper in Compacted Na-Montmorillonite Sand Mixtures F. King et al Corrosion Science, Vol. 33, No. 12, pp. 1979-1995, 1992" som bygger på rapporten "A Mechanistic Study of the Uniform Corrosion of Copper in Compacted Clay-Sand Soil Litke Ryan King AECL-10397 1992".

Det som nämns i artikeln på sidan 1991 nedtill är att mer än hälften av kopparen finns i korrosionsprodukterna på ytan:

"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."

Detta utvecklas lite mer i rapporten på sidan 10:

"The amount of copper in the form of adherent corrosion product and precipitate ( $\Delta w_p$ ) was estimated by subtracting the total amount of copper in the buffer ( $\Delta w_b$ ) from the overall weight loss of the coupon ( $\Delta w$ ). The fraction ( $\Delta w_p / \Delta w$ ), which represents the proportion of precipitated copper, varied from test to test. In 1- and 2-month tests at 50°C,  $\Delta w_p / \Delta w$  was as high as 0.95, indicating that only 5% of the dissolved copper diffused into the buffer. In general, the amount of copper in the buffer increased with exposure time, although in most of the experiments more than 50% of the dissolved copper had precipitated on or near the coupon. For longer exposure periods, however, most of the dissolved copper may diffuse through the buffer rather than precipitate at the interface."

Hur detta kan omvandlas till en faktor att multiplicera halten i leran med för att få den totala mängden korroderad koppar är för mig något oklar. Men i det arbete som genomförts i Kanada har det funnits en ambition att göra en uppskattningen. I de resultat som kärnavfallsbolaget SKB presenterat i rapporten SKB TR-20-14 saknas helt ambitionen att göra en sådan uppskattning trots att den är viktig för att kunna värdera bolagets slutsats att all

korrosion under 20 år i LOT-paketens orsakats av syrgas instängd i försökpaketet.

#### Avslutande kommentarer

MKG avser fortfarande och i närtid inkomma med ett andra bidrag till SSM:s kvalitetsgranskningars arbete som utgår från frågeställningar som väckts vid en genomgång av rapporten SKB TR-20-14.

Rörande SSM:s med att hantera stora filer i diariet kan MKG informera myndigheten att föreningens e-postsystem inte har begränsningar på hur stora filer som kan tas emot.

Bästa hälsningar,

Johan

(1) Presentation är intressant att ta till sig som helhet och känns fortfarande väldigt aktuell över tio år senare. Det finns förmodligen även annat från seminariet som fortfarande är aktuellt. Här är två nyheter på MKG:s hemsida om seminariet:

<http://www.mkg.se/inga-svar-pa-karnavfallsradets-kopparkorrosionsseminarium>

<http://www.mkg.se/kth-forskarna-skickar-extra-material-till-korrosionsseminariets-expertpanel>

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Johan Swahn

Kanslichef

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28 okt. 2020 kl. 14:25 skrev Strömberg, Bo <[Bo.Stromberg@ssm.se](mailto:Bo.Stromberg@ssm.se)>:

Hej Johan

Vi har tittat lite mera i detalj på skrivelsen och har några frågor:

En fråga under punkten nr 4 för att förstå era synpunkter kring korrosion vid olika redoxförhållanden.

“MKG would like to strongly stress that the way SKB continually keeps stressing that a number of copper corrosion products can only occur if the environment has been anoxic is fundamentally flawed.”

Ska det inte vara: “...can only occur if the environment has been **oxic** is fundamentally flawed.” Det vore också bra att få reda på vad menas med “a number of corrosion products” dvs. vilka faser avses?

“MKG is of the understanding that it should be clear by now that SKB has no interest in improving the scientific understanding of this issue as it allows the company to claim that all copper corrosion is anoxic, while in fact it is much more likely that very little of the copper corrosion in experiments carried out in hard rock laboratories is anoxic.”

Samma fråga här, borde det inte vara “...the company to claim that all copper corrosion is **oxic**, while in fact it is much more likely that very little of the copper corrosion in experiments carried out in hard rock laboratories is anoxic

## En fråga under 2. Om FEBEX

There was quite intensive corrosion ( $\approx 100 \mu\text{m}$  and pitting) on copper coupons after 18 years in the FEBEX experiment as reported in the report "FEBEX-DP Metal Corrosion and Iron-Bentonite Interaction Studies, P. Wersin & F. Kober (eds.), Arbeitsbericht NAB 16-16, Nagra, October 2017"

Formuleringen är tvetydig huruvida  $100 \mu\text{m}$  avser gropfrätningsdjup eller allmän korrasjon med ytterligare tillskott från gropfrätning. Det föregående alternativet verkar stämma bäst med sid 22, sid 192, sid B-5, B-20 i Nagra Arbeitsbericht NAB 16-16).

## En fråga under 3. Om LOT A2

"The calculated corrosion rate is 2-4  $\mu\text{m}$  per year for a position representing clay zone 15 and to this number an amount (up to times 4?) should be added to correspond to the corrosion products left on the copper surface."

Finns en förklaring eller referens som motiverar up to times 4?

I övrigt kan jag meddela att vi fått problem med vissa filer i diariet som ska skickas ut. Det beror på att filerna är så stora att systemet har problem att hantera dessa. Jag hoppas att detta går att åtgärda så snart som möjligt

Bästa hälsn Bo



**Bo Strömberg, PhD**  
Strålsäkerhetsmyndigheten  
**Swedish Radiation Safety Authority**

Analyst, safety assessment

Avd. för radioaktiva ämnen  
Dept. of Radioactive Materials

SE-171 16 Stockholm

Så här behandlar myndigheten dina personuppgifter:  
[Behandling av personuppgifter](#)



MKG input to  
SSM re...ed).pdf



Presentation  
Szakal...09.pdf



A Mechanistic  
Study...92.pdf



A Mechanistic  
Study...92.pdf



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

## **Thermodynamics and kinetics of copper corrosion in oxygen free water**

**Ph. D. Peter Szakálos, KTH  
Associate Prof. Olle Grinder, KTH**



## Background

**It was known already 30 years ago that copper was not thermodynamically immune in pure O<sub>2</sub>-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 <sup>1-3</sup>, which easily converts to oxides, especially upon exposure to air <sup>1</sup>.**

- 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)



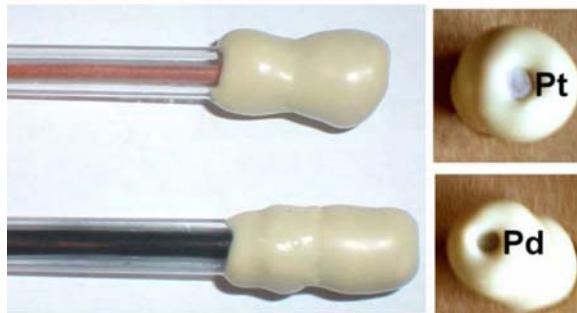
**SKB has referred to four papers during 23 years which are claimed to support the assumption of zero copper corrosion in O<sub>2</sub>-free water.**

- Two papers in *Corrosion Science*, 1987 and 1989 which we disregard since O<sub>2</sub> 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](http://www.karnavfallsradet.se)

**Only one study (attempt) has been performed during the latest 23 years to repeat Hultquist's experiment: SKI 95-72<sup>4</sup>**

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



**That specific experiment did indeed indicate that copper corrodes in O<sub>2</sub>-free water.**

**However, no follow-up was ever done.**

<sup>4</sup> 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 O<sub>2</sub>-free  
brackish water)



En av regalskeppet Kronans kanoner omedelbart efter bärgningen.

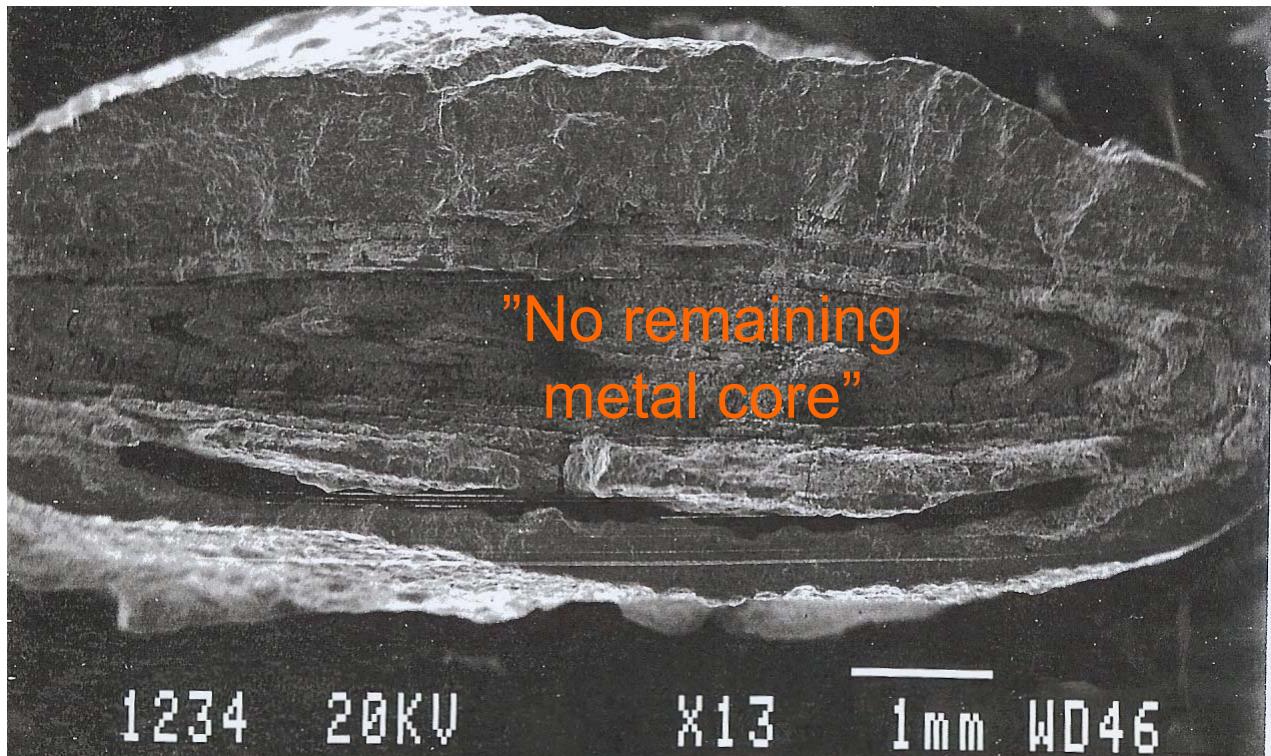
**The corrosion of bronzes differs fundamentally from that of copper. An enrichment of passivating tin forms on the bronze surface that strongly reduces the corrosion rate in aqueous environments, this was known already 30 years ago.**

# 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



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

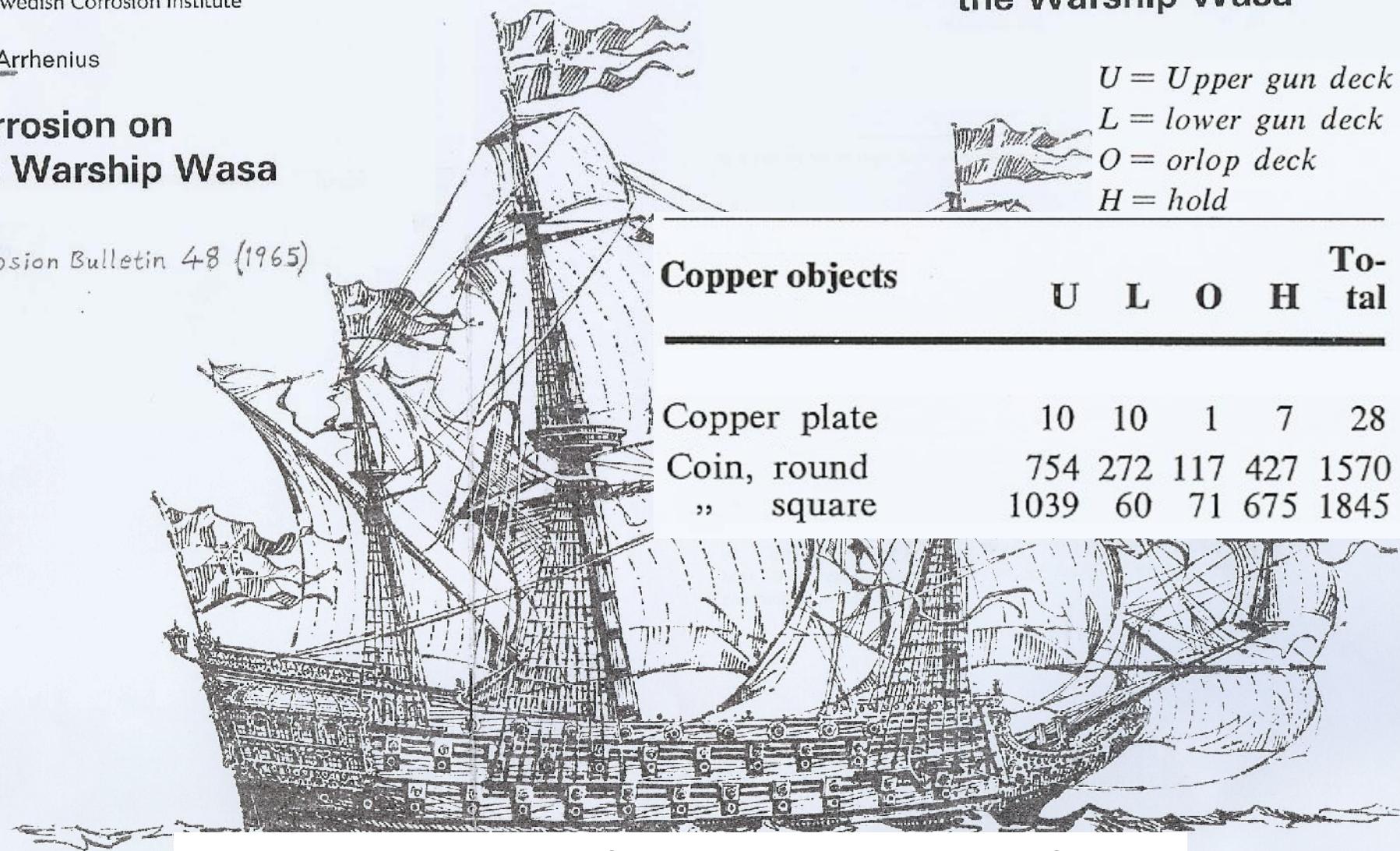
Copper coins on *Kronan* were more corroded than on *Wasa* and several *Kronan*-coins had no remaining metal core left



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*

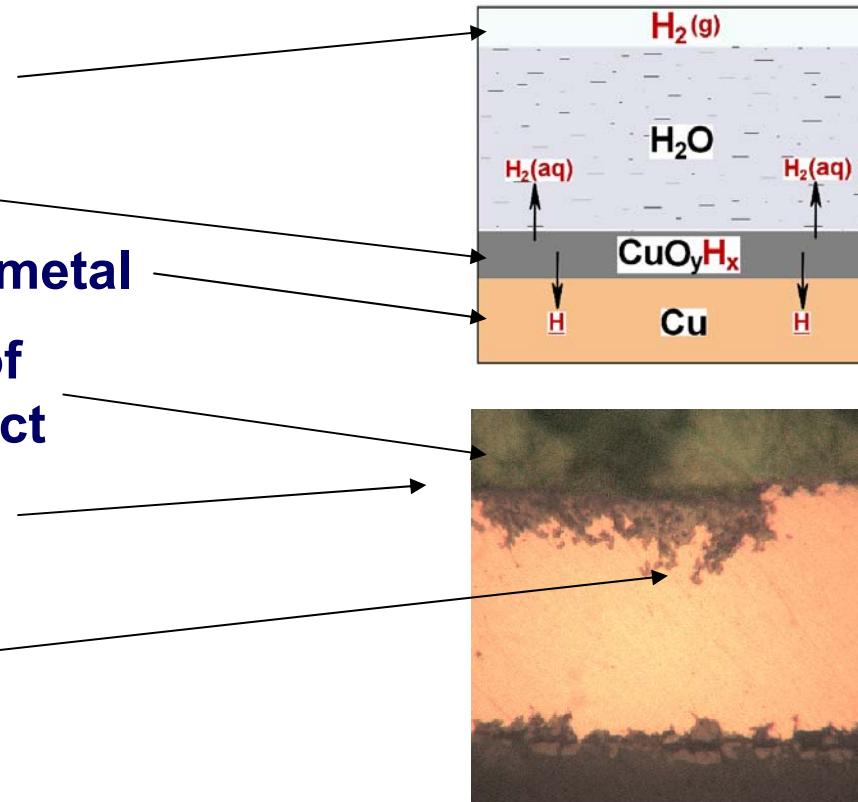
Copper objects	U	L	O	H	Total
Copper plate	10	10	1	7	28
Coin, round	754	272	117	427	1570
" square	1039	60	71	675	1845

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

# Our corrosion results

The presence of copper corrosion on pure O<sub>2</sub>-free water have been verified by following observations:

- H<sub>2</sub>-gas detection
- Weight gain
- H-uptake in copper metal
- Chemical analysis of the corrosion product
- Visual inspection
- Metallographic examination



# STATOR COOLING WATER



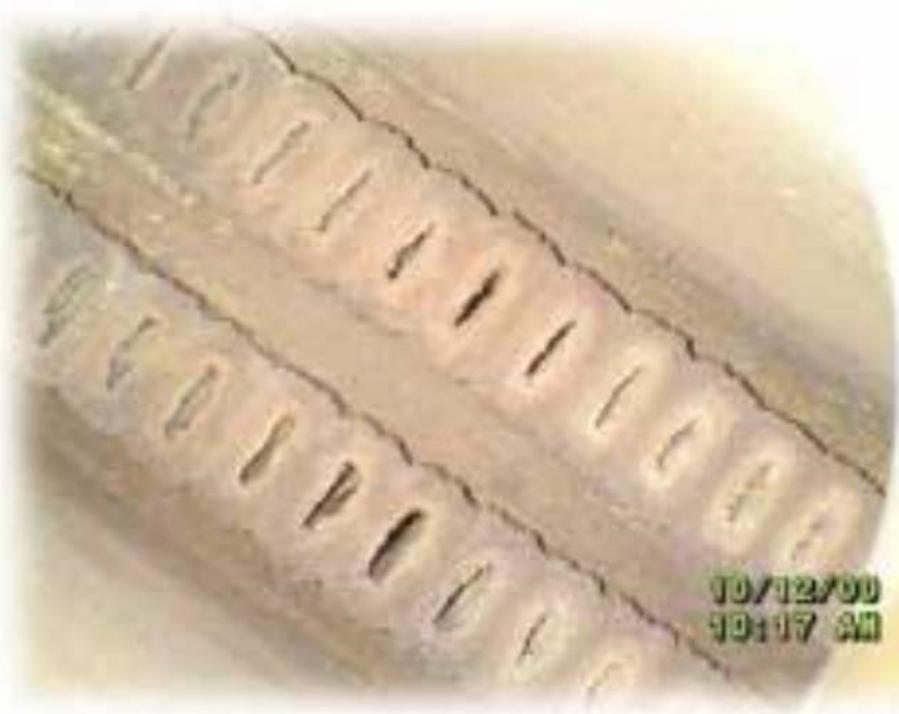
Corrosion in the stator cooling system of power generators is a primary source of maintenance costs and plant downtime.

Copper corrosion in O<sub>2</sub>-free water is a well known industrial problem.

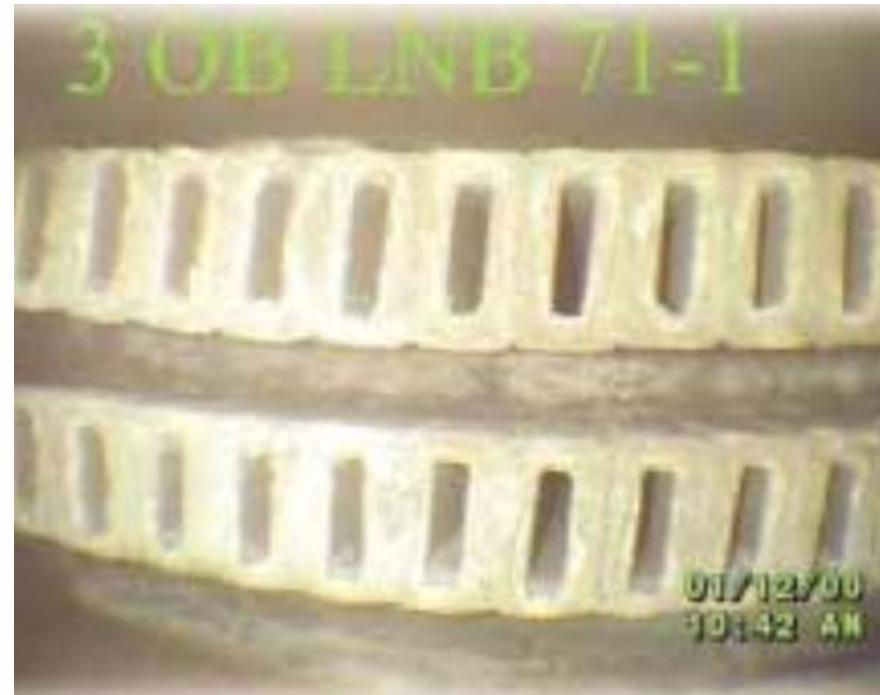
All copper cooling system for power generators and accelerators (CERN etc) corrodes (0.5-10µm/y)

Environment: Deionised and degassed water around 70°C

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

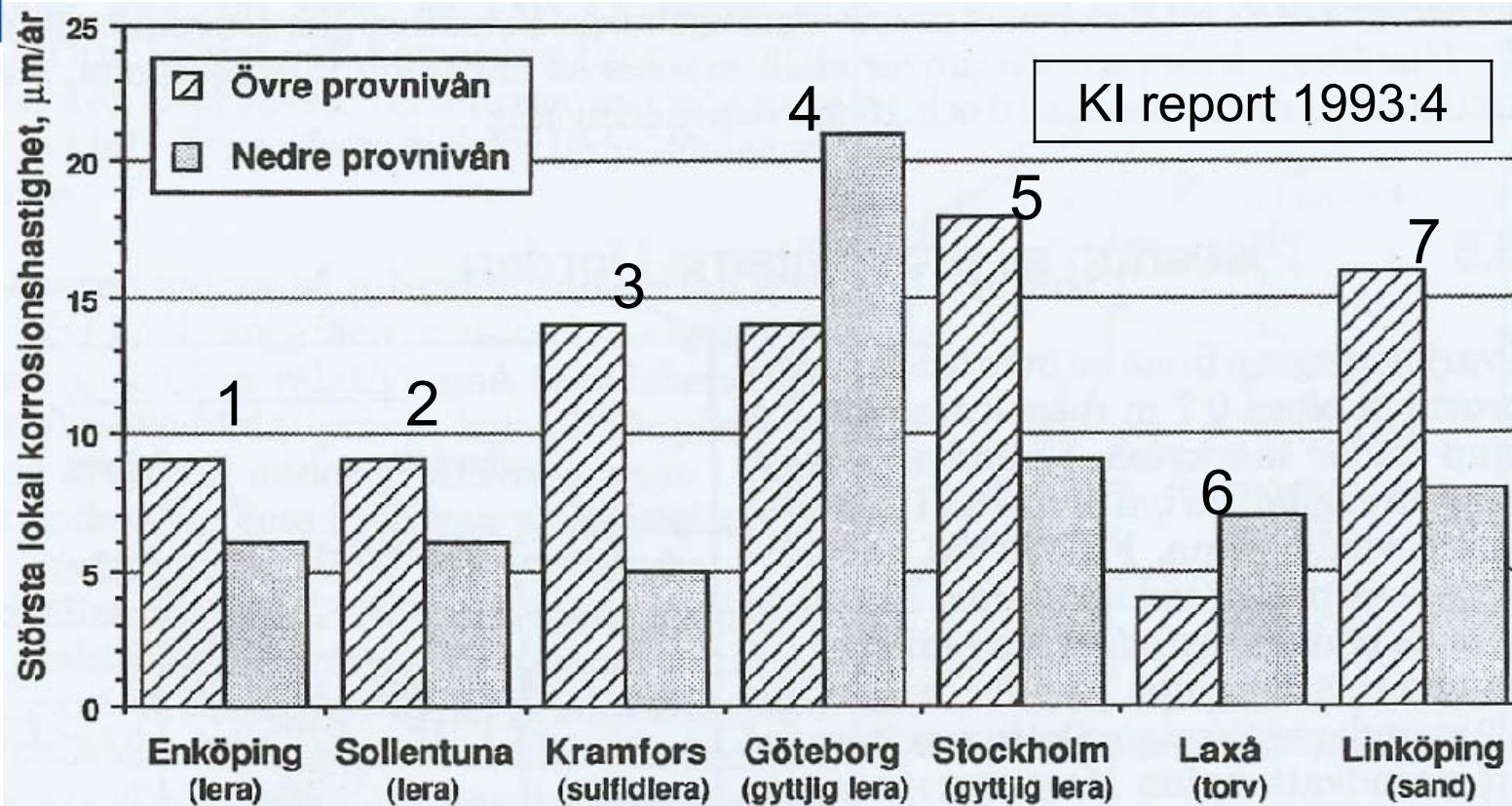


*Figure 1. Partial plugging by copper corrosion products (oxides and hydroxides) prior to cleaning of water-cooled generator at SONGS 2. Photo courtesy of EPRI*



*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



Figur 3. Största lokal korrosionshastighet på koppar i olika jordarter efter 7 års exponering på Korrosionsinstitutets provplatser.

**Low redoxpotentials were recorded in test sites 2, 3, 4 and 5, which indicate O<sub>2</sub>- 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 <sup>1)</sup>	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

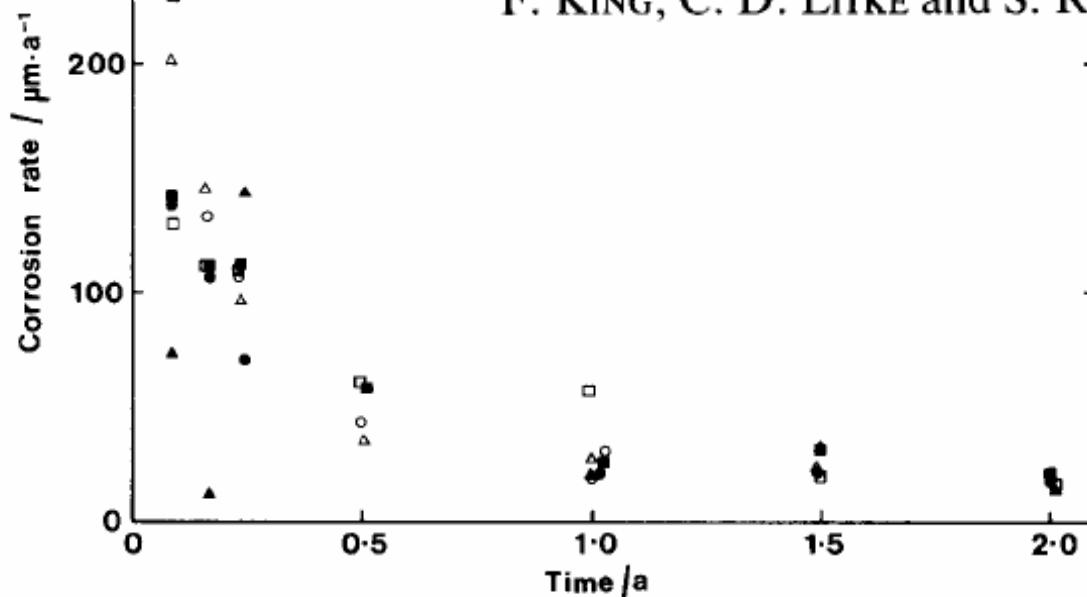


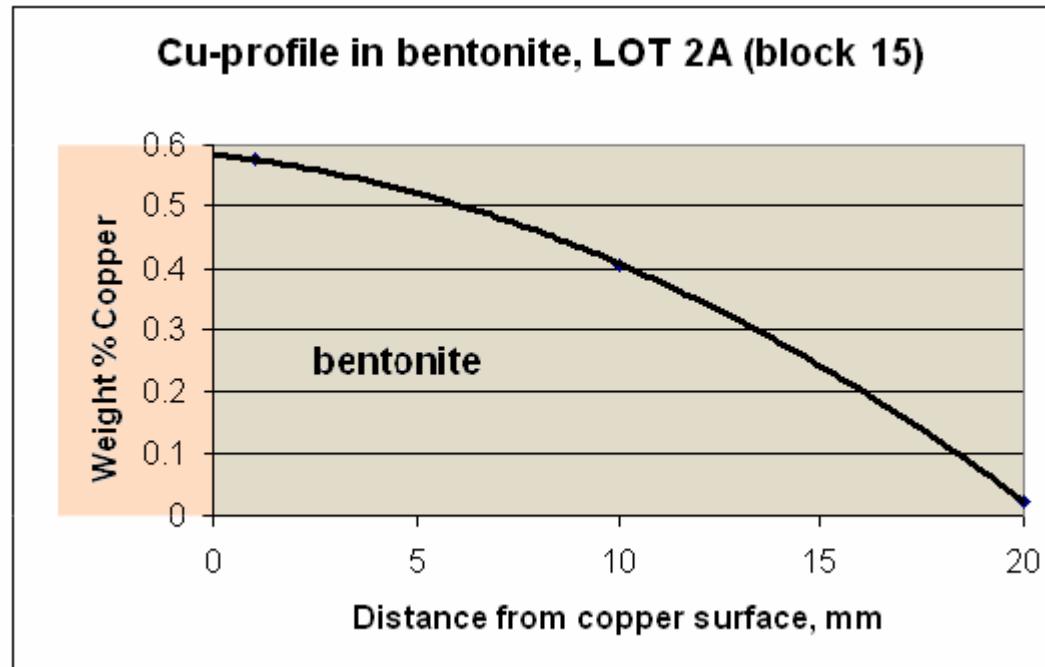
FIG. 8. Copper corrosion rates determined from weight loss of coupon in contact with compacted buffer material in absence of  $\gamma$ -radiation. ● 50°C, 1.45 g  $\text{cm}^{-3}$  buffer density; ■ 50°C, 1.65 g  $\text{cm}^{-3}$ ; ▲ 50°C, 1.79 g  $\text{cm}^{-3}$ ; ○ 100°C, 1.45 g  $\text{cm}^{-3}$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

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

On page 1991, it was concluded that “ $\text{O}_2$ -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  $\mu\text{m}/\text{y}$  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  $\mu\text{m}/\text{y}$  (pitting corrosion not taken into account).



# Microbially accelerated corrosion

(MICROBE laboratory in Äspö)

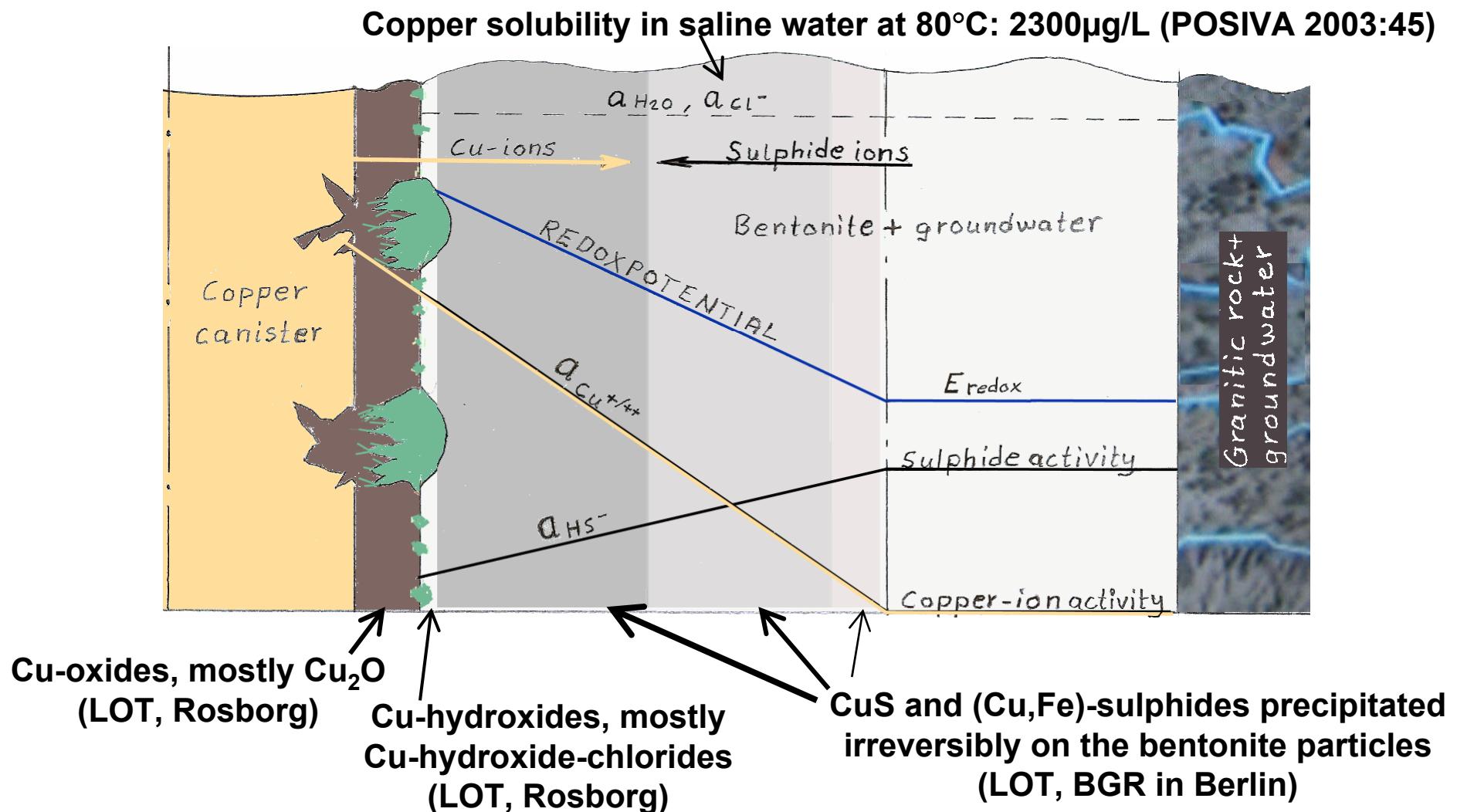
Bacterial activity in the repository environment produces both sulphide (from sulphate) and acetate (from  $\text{CO}_2$ ,  $\text{H}_2$ ), thus affecting the chemistry, redoxpotential and copper corrosion.

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

- 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  $(\text{Cu},\text{Fe})\text{S}$ , thus driving the microbial production of sulphide.
- The copper corrosion are consequently accelerated with precipitation of Cu-sulphides and  $(\text{Cu},\text{Fe})$ -sulphides in the bentonite (Confirmed by SKB's LOT-project).

<sup>5</sup> L. Hallbeck, K. Pedersen, Applied Geochemistry 23, p.1796 (2008)

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



# Intergranular corrosion (IGC) of copper

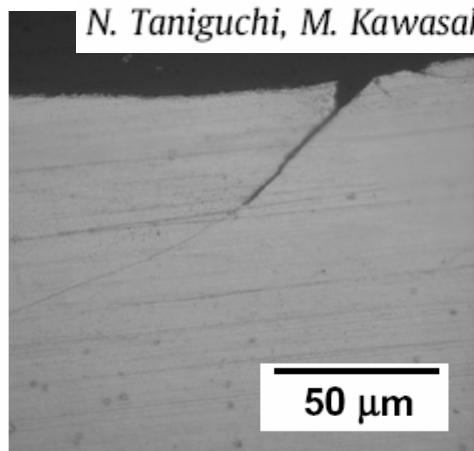
*Electrochemical and Solid-State Letters*, 11 (4) G15-G18 (2008)  
1099-0062/2008/11(4)/G15/4/\$23.00 © The Electrochemical Society

## Rapid Intergranular Corrosion of Copper in Sulfide-Polluted Salt Water

F. M. Al Kharafi, I. M. Ghayad, and B. G. Ateya<sup>\*,\*</sup>

“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 O<sub>2</sub>



0.001M-Na<sub>2</sub>S

Slow Strain Rate Testing, SSRT:  
Synthetic seawater 80°C without O<sub>2</sub>  
Extension rate: 8.3E-7 s<sup>-1</sup>

Both Forsmark and Olkiluoto, groundwater without O<sub>2</sub>

# Stress Corrosion Cracking, SCC

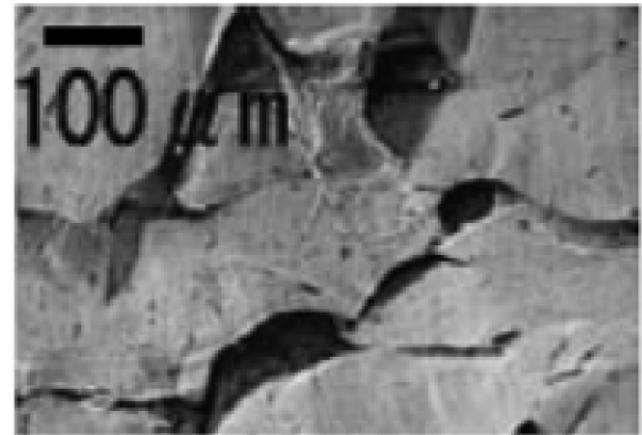
European Commission: 5'th EURATOM FRAMEWORK PROGRAMME 1998-2002,  
COBECOMA, final report (2003). B. Kursten, L. Werme et al. Page 166:

"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:

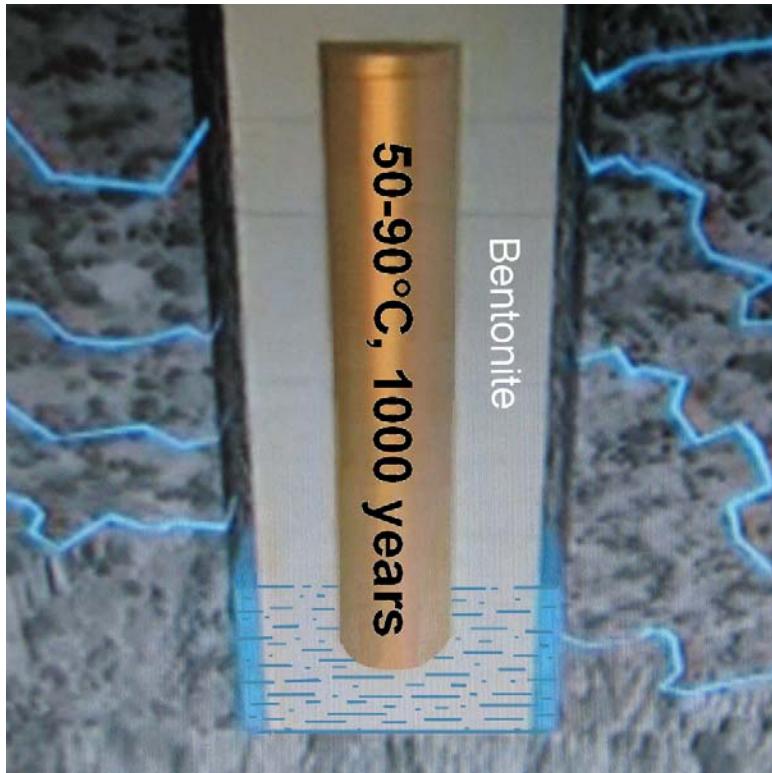


SCC at 80°C on OFHC-Copper with 45ppm P

**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 µm/year depending on the temperature.**

**The corrosion rate of copper in wet bentonite or soil has been found to be 1-30 µm/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.**



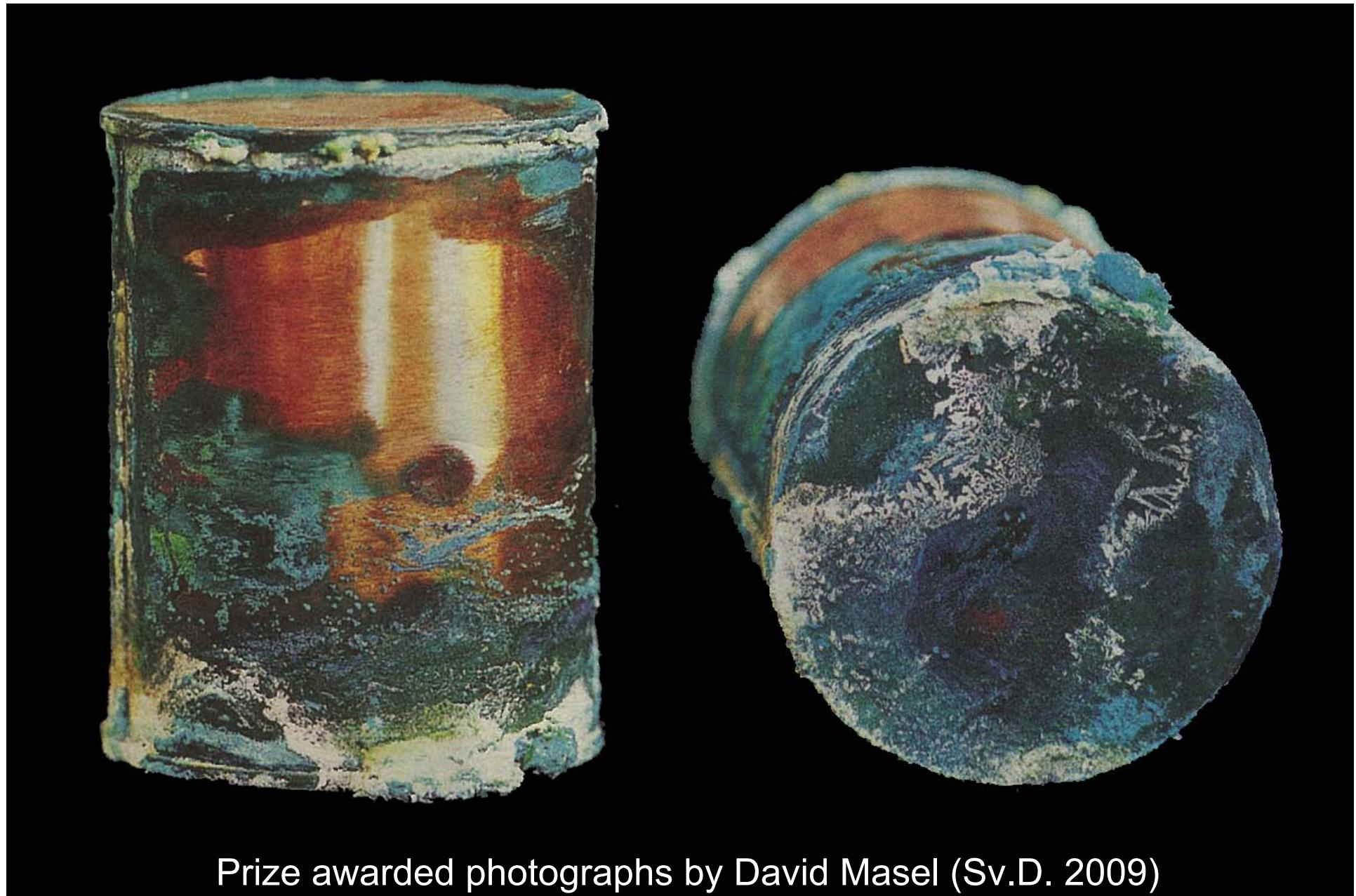
## Conclusions cont.

**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)