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SSM's Workshop on the Review of SKB's License Application for a Spent Nuclear Fuel Repository, at Rånäs Castle in Sweden, 21-23 May 2012

SSM's Initial Review Phase for SKB's safety assessment SR-Site:

2.2 Corrosion of copper canister

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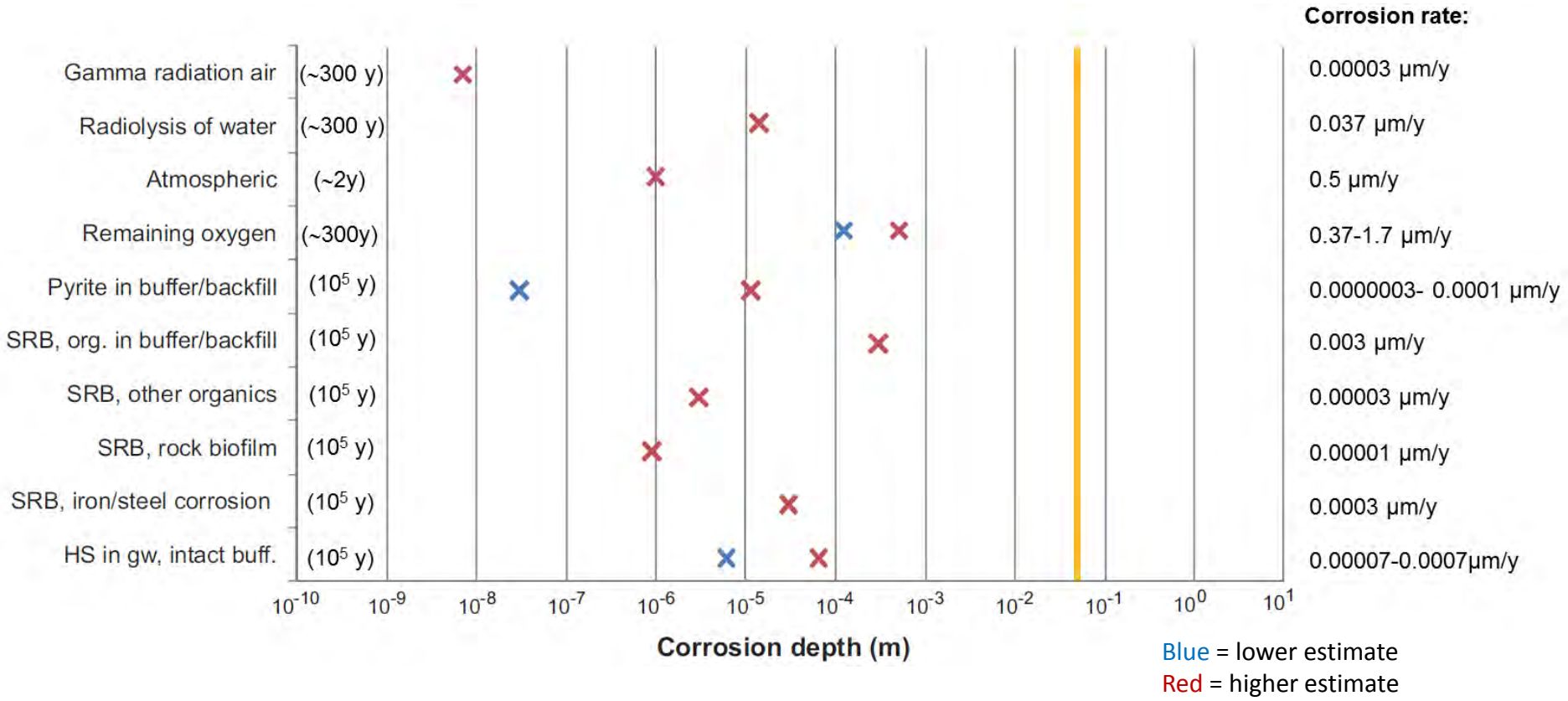
Corrosion during 10^5 years based on data from SKB´s safety analysis (TR-10-67)



Total corrosion less than 1 mm during 100.000 years?

P. Szakálos and S. Seetharaman

What will happen with an entrapped gas volume in a deposition tunnel at 450 meter depth in Forsmark?

The surrounding groundwater in the bedrock contains trace gases. This means that the tunnel gas volume will be a sink for dissolved gases in the groundwater.

The measured dissolved gases in the Forsmark groundwater (TR-10-58 and TR-10-39) are: H_2 = 10^{-3} to 10^{-2} mM, CH_4 = 5×10^{-3} to 0.2 mM, sulfide (as H_2S) = 10^{-4} to 0.12 mM,

The concentrations in a gas phase in equilibrium with respective compound at a total pressure of one bar are according to Henry´s law, 0.3 to 3 mbar H_2, 1 to 50 mbar CH_4, 10^{-5} to 6×10^{-3} mbar H_2S.

The H_2S-content can vary considerably in the groundwater and can locally be as high as 3 to 30 mM, or 0.15 to 1.5 mbar H_2S, as measured in Olkiluoto (POSIVA 2007-04).

Some of these trace gases, such as H_2S, will effectively be scavenged/consumed by copper and this will promote the microbial activity, i.e. accelerated sulfate reduction by SRB.

Bell Laboratories has studied a similar atmosphere as expected during the initial period, air polluted with 1.7 ppm H_2S (1.7×10^{-3} mbar H_2S) and sub ppm levels of other trace gases, which shows that copper, already at 40°C and 69% RH, corrodes more than 100 µm per year The corrosion product consisted of a non-adherent scale with Cu_2O closest to the metal and Cu_2S (or Cu_xS) on the top. The corrosion rate is found to be linear, i.e. no protective "passive" film develops in such an environment.

K. Demirkan et al. *J. of The Electrochemical Society,* 157,1, C30-C35 (2010)

SKB has omitted the atmospheric corrosion with trace gases such as H_2S in the safety analysis

P. Szakálos and S. Seetharaman

Ground water evaporation and salt precipitation
”The sauna effect”

INPUT: *The water inflow <0.01 l/min in 99.9% of the deposition holes in the Forsmark (SKB TR-06-102).*

Assumptions:

Water flow:

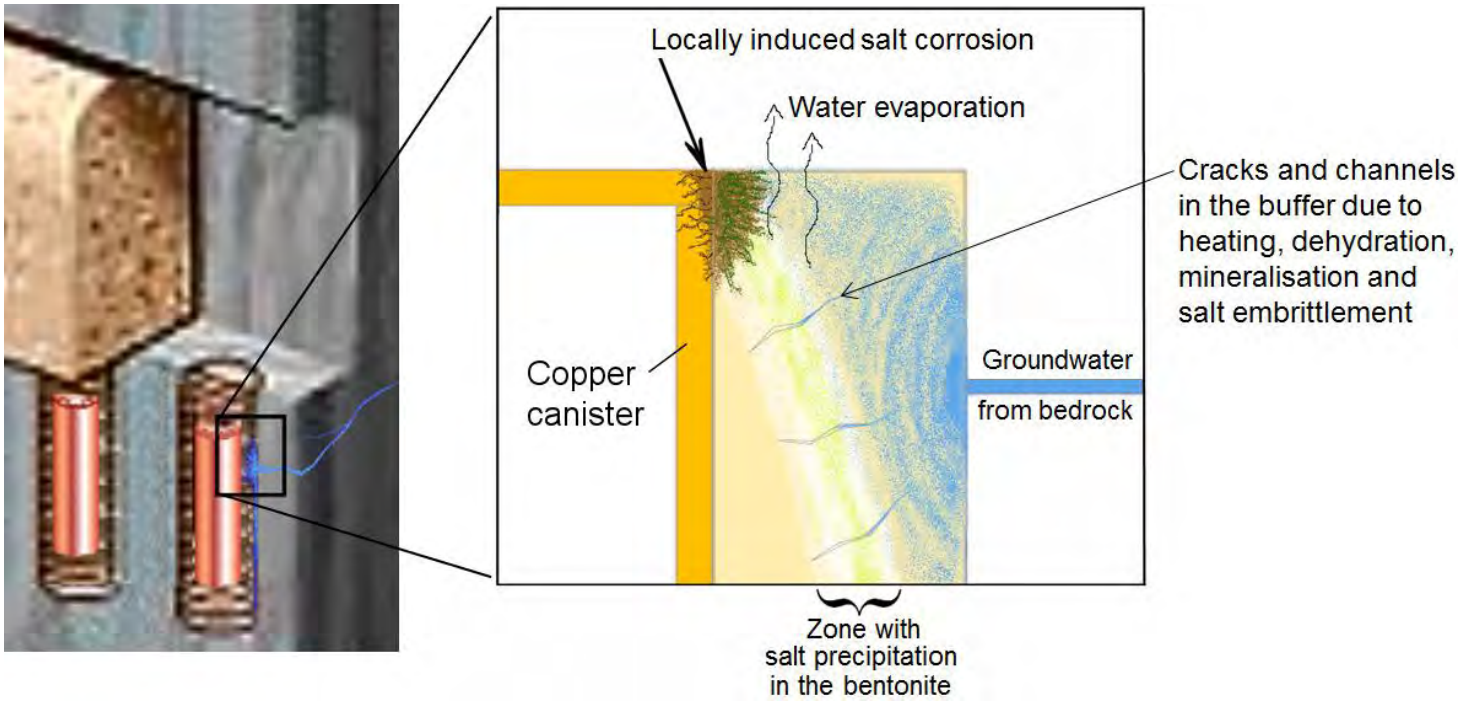
Some deposition holes will experience half that inflow rate, 0.005 l/min. ⇒ Corresponds to an groundwater inflow of 2.6 m^3/year.

Water evaporation and Salt Deposition:

Each canister evolves 1700 W as heat ⇒ Water evaporation, a flow from the deposition holes to the tunnels ⇒ the different salts will stay in the deposition hole.

Ground water evaporation and salt precipitation ”The sauna effect”-Consequence

Total salt content in Forsmark groundwater is around 0.95 wt-%, ➡ 16 kilo salt/deposition hole/year ➡ one cubic meter of salt or 2500 kg may precipitate in such a deposition hole within 100 years.



Only a few metals can resist chlorine- and sulfur salt deposition during heating and water evaporation, with or without oxygen. In the industry, palladium alloyed titanium or tantalum is used in such environments.

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Copper dissolution corrosion in saline anoxic water

Linear corrosion rate at 80-120 µm/y

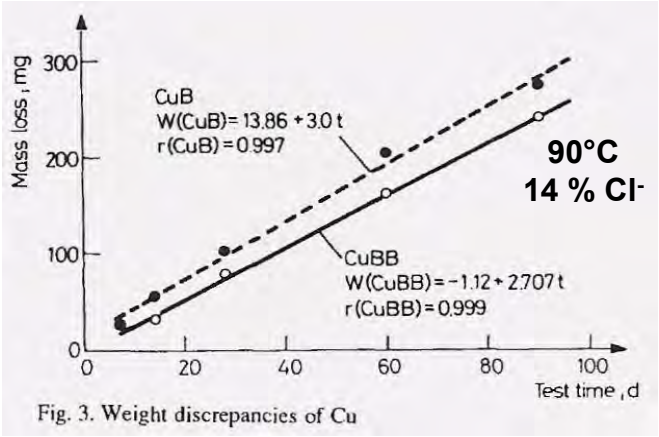
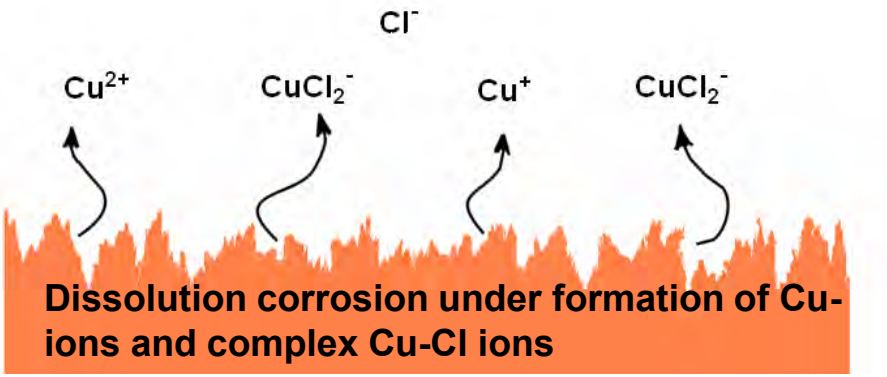
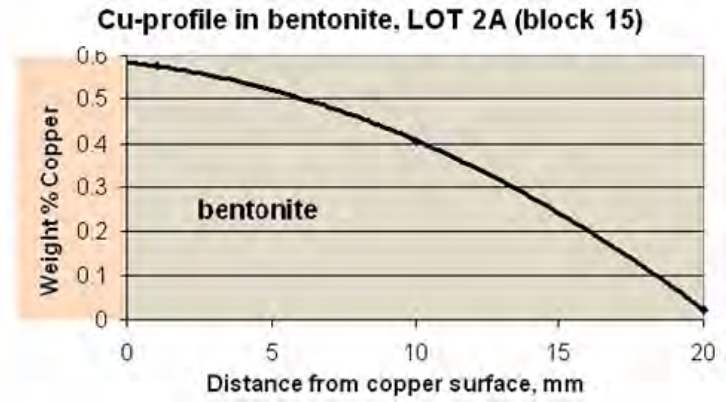


Fig. 3. Weight discrepancies of Cu



J. of Radioanalytical and Nuclear Chem. Vol.182, No. 2, p 281 (1994)

...and precipitation in bentonite (an effective sink for copper ions/ corr. products) as observed in the LOT A2 project, TR-09-29 page 228-233



SKB has omitted copper dissolution/ precipitation corrosion in the safety analysis

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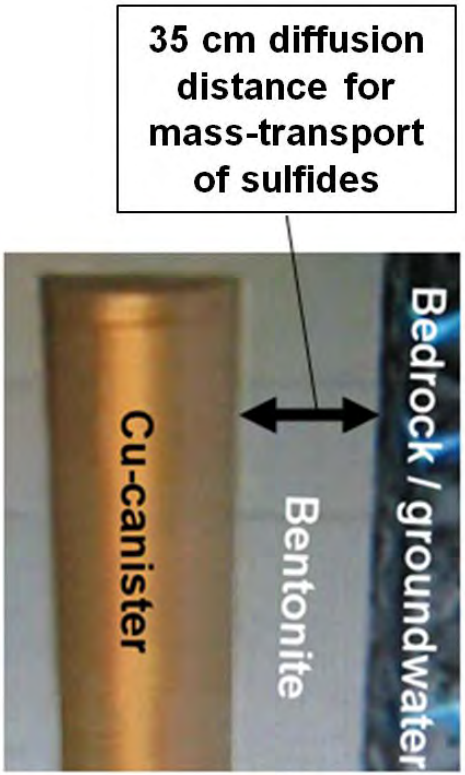
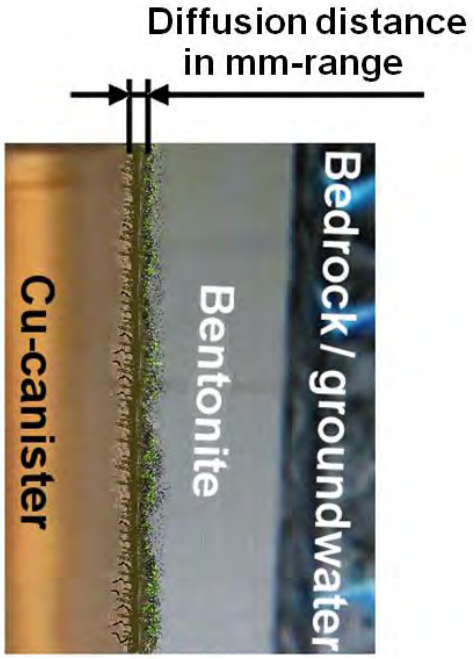
The KBS-3 model:



All relevant copper corrosion processes are calculated by diffusion through an buffer in an ”ideal state”, water saturated and pressurised

Reality:



- **Copper dissolution as Cu^{2+} och $CuCl_2^-$**
- **The bentonite surface acts as a sink for these ions. Different crystalline corrosion products precipitate on the bentonite**
- **The chloride ions get released and the corrosion process continues**
- **The bentonite and copper barriers break down each other and the corrosion continues with short diffusion distances**

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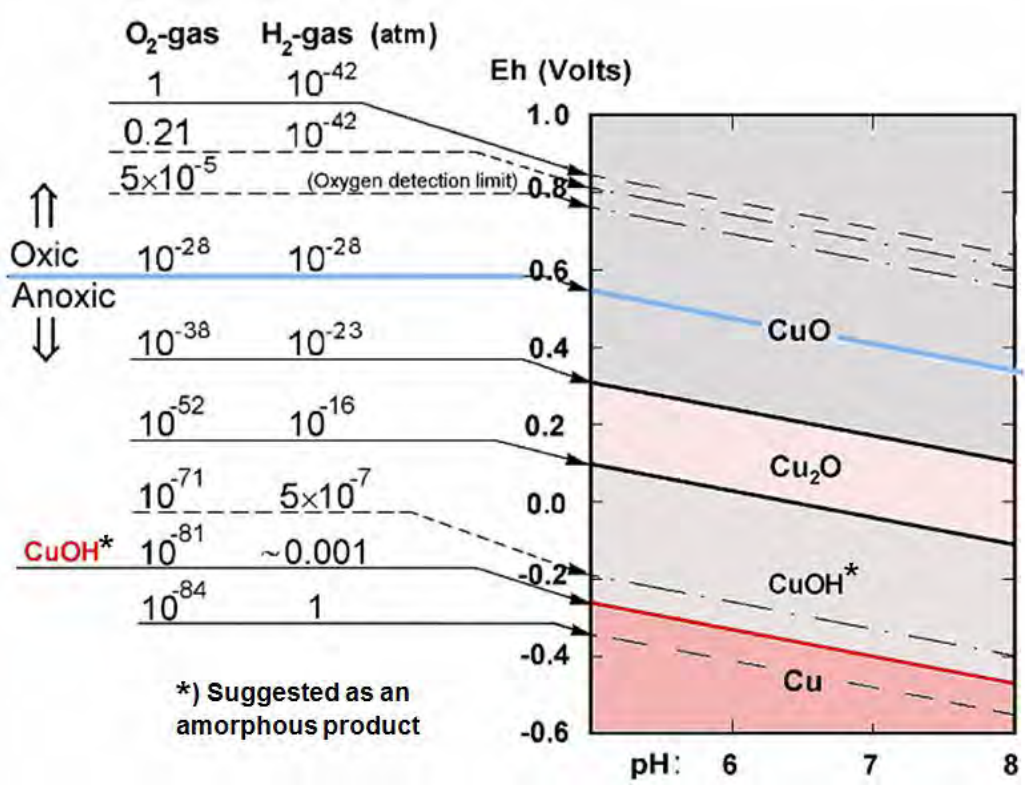
Anoxic copper corrosion



- Copper is not immune in pure gas free water, both mono- and bivalent oxides are stable

Mechanism of corrosion in pure water is of prime importance since it may explain why copper corrodes more than expected. For instance, in copper cooling systems in accelerators, large generators and ITER, copper corrosion is a real problem. It is not difficult to assemble perfectly air (oxygen) tight metallic couplings but it is impossible to make systems hydrogen tight. This is the answer to the problem, as long as hydrogen can escape (or be consumed) copper corrosion is expected, also in pure water.

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Stray (earth) current at the Forsmark site

The Fenno–Skan 1 was installed as a monopolar system with a maximum transmission rate of 550 megawatts (MW) at a voltage of 400 kV. Fenno-Scan 2 was installed 2011 with increased energy transport capacity to 800 MW. Depending on the imbalance between the two cables the stray current and corresponding corrosion could be higher or lower than that observed with the monopolarFenno–Skan1.

- It is known from failure cases that the corrosion rates due to earth currents could, under certain circumstances, reach millimeters per week. Severe crevice and pitting corrosion due to stray/earth current was observed on stainless steel borehole equipment already after 10 days operation at 360 m depth at the Forsmark site, see SKB P-05-265.

- **SKB has disregarded the risk for corrosion caused by stray currents.**

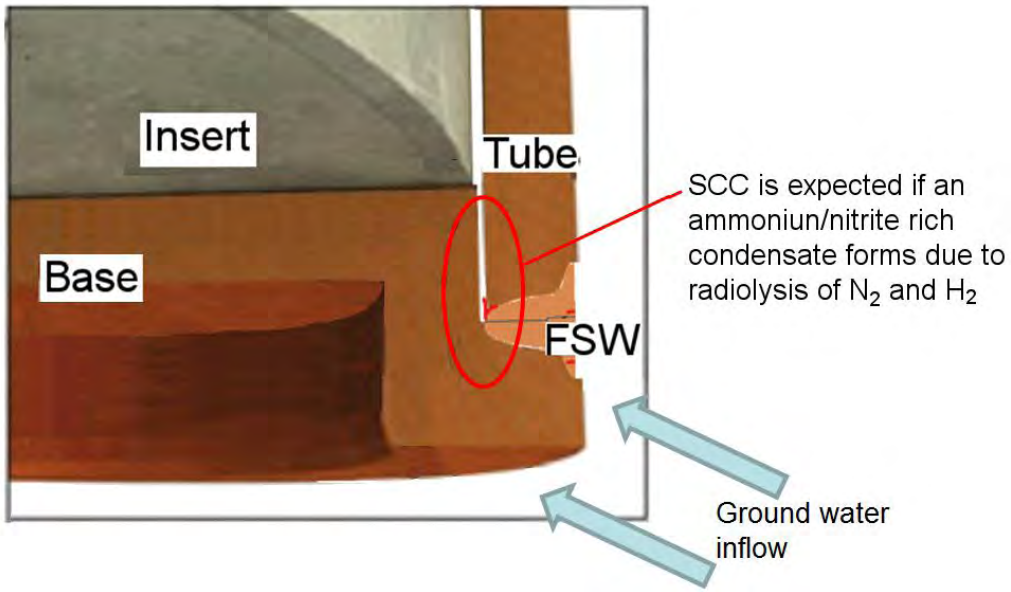
Stray current failur case on stainless steel equipment from the Forsmark site, see SKB P-05-265

Stress Corrosion Cracking

TR-11-01 p.226: ”Stress corrosion cracking of the copper canister is neglected due to the combined effect of very low (if any) concentrations of SCC promoting agents and the insufficient availability of oxidants.”

Two scenarions where the basic prerequisite for SCC may occur:

- Ammonium and nitrite induced SSC inside the canister due to radiolysis. The formation of those species is expected in an N_2-H_2-H_2O atmosphere[1].
- Sulphide induced SCC du to accumulation of salts (inc. sulphides) due to ”the sauna effect” in the deposition hole. At higher concentrations of sulfide, *also during anoxic conditions*, SSC is indeed expected in OFHC-copper with 45ppm phosporus[2].



The statement above regarding SCC in TR-11-01 is obviously wrong and more experimental data is needed.

1) H. Karasawa et al. Int. J. of Radiation, Applications and Instrumentation. Part C. Radiat. Phys. Chem. Vol. 37, No. 2, pp. 193-197(1991)
2) N. Taniguchi and M. Kawasaki, Journal of Nuclear Materials 379, p. 154 (2008)

Embrittlement of copper due to sulfur grain boundary diffusion and sulfide precipitation

CT, constant load, 3 week exposure at RT

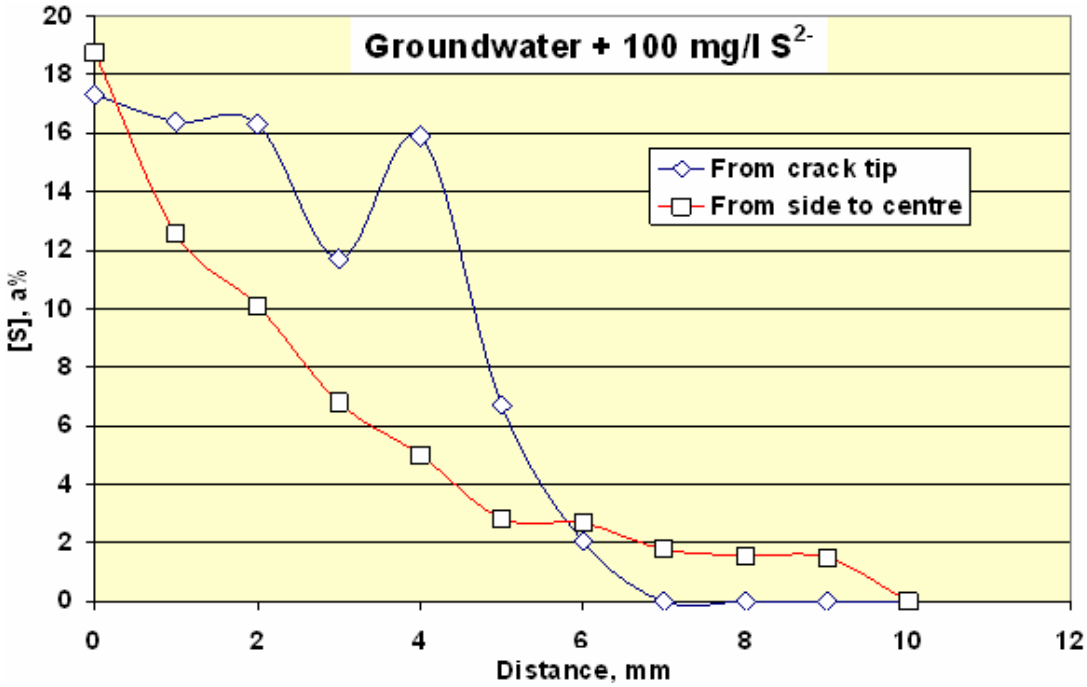
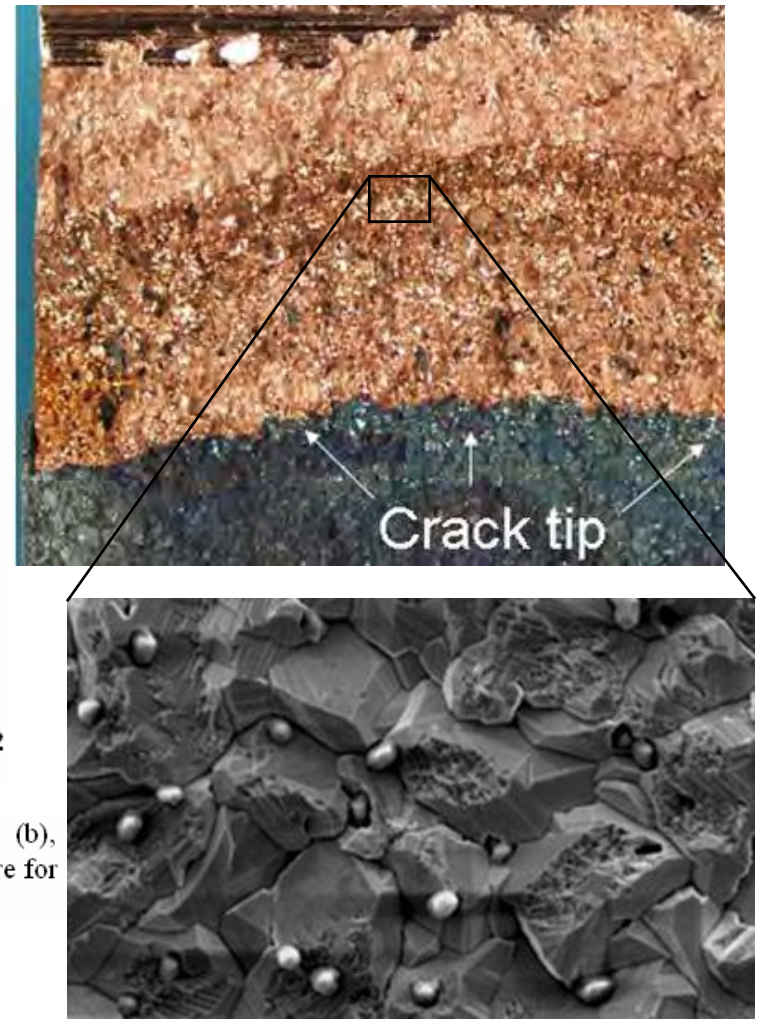


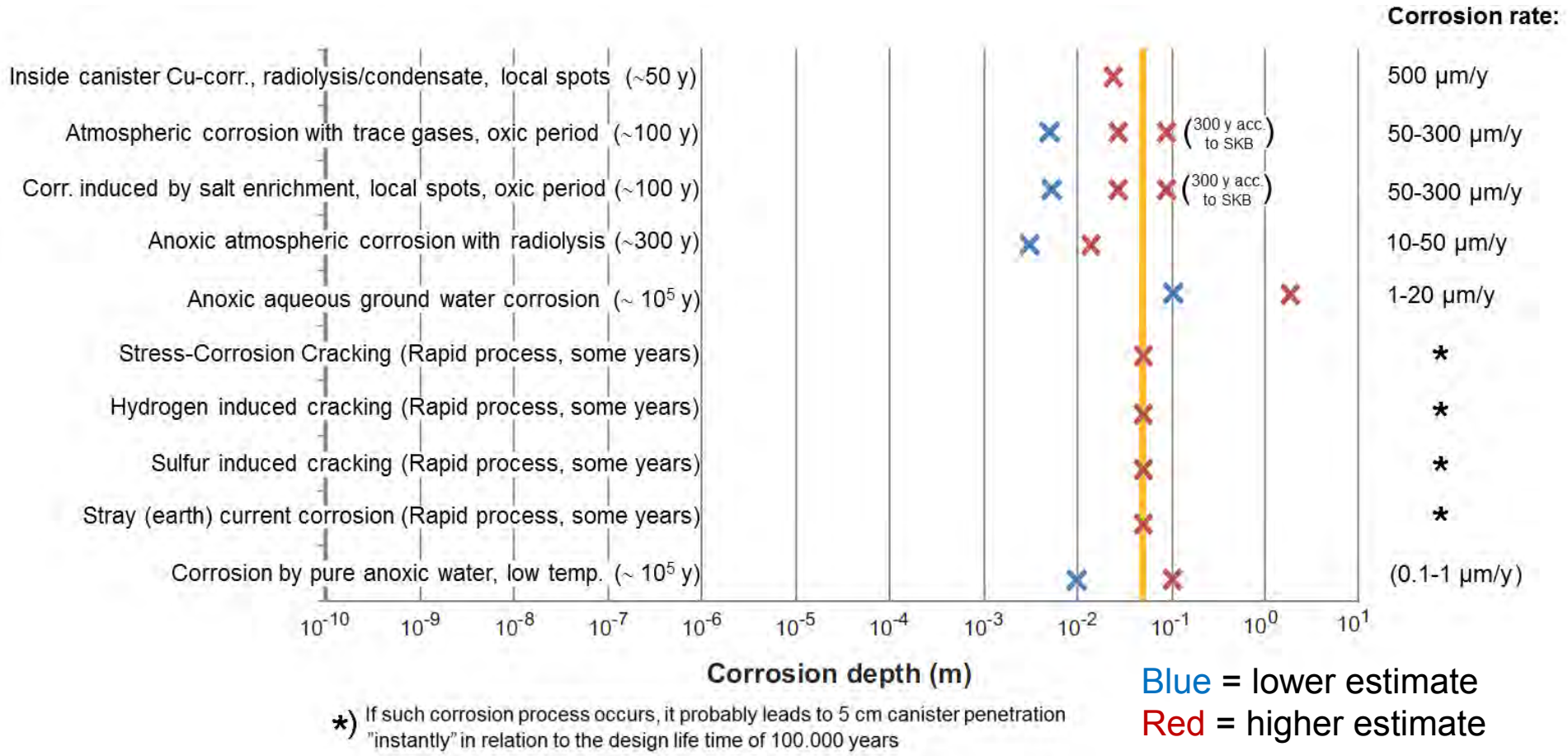
Figure 7. Atomic percentage of sulphur as a function of distance (a), ahead of the crack tip and (b), from side towards the centre of the specimen at a distance of 2 mm from the crack tip. Exposure for three weeks to groundwater with 100 mg/l sulphide.



REF. Arilahti E., Lehtikuusi T., Olin M., Saario T. & Varis P.; Evidence for internal diffusion of sulphide from groundwater into grain boundaries ahead of a crack tip in a CuOFP copper. 4th international workshop on long-term prediction of corrosion damage in nuclear waste systems. Brugges, Belgium, June 28 – July 2, 2010.

P. Szakálos and S. Seetharaman

Corrosion in a proposed Forsmark repository during 10^5 years according to our estimations



*) If such corrosion process occurs, it probably leads to 5 cm canister penetration "instantly" in relation to the design life time of 100.000 years

Blue = lower estimate
Red = higher estimate

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Requests for more information

General;

- Is it expected that an entrapped gas volume in a deposition tunnel at 450 m depth in Forsmark has no exchange with the surroundings?
- Is there no communication/water transport between deposition holes and the tunnel during the initial period when the bentonite is not saturated with water? Or will there be a redistribution of water and enrichment of salt in the deposition holes, in the bentonite, on the copper surface and finally, when the salt resolves, in the water?

Copper corrosion mechanisms;

- Atmospheric corrosion by trace gases (Not considered)
- Corrosion by precipitated salts (Considered, but neglected)
- Corrosion caused by dissolution of copper in water and precipitation in the bentonite (Not considered)
- Corrosion caused by stray currents (Considered but neglected)
- Anoxic corrosion (Considered but neglected)

Copper embrittlement mechanisms; (Considered but neglected)

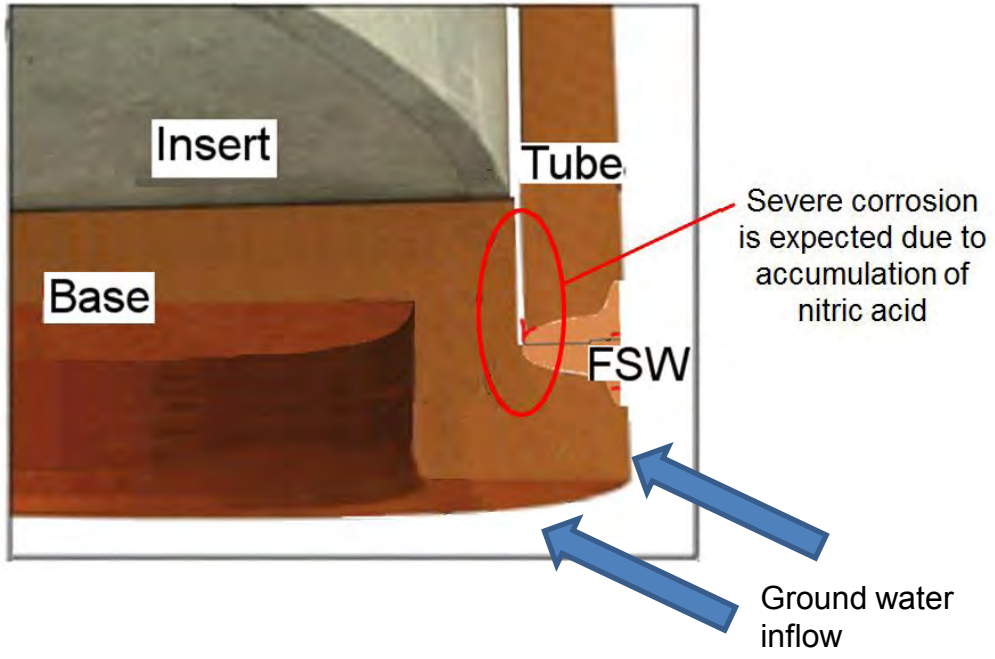
- Stress corrosion cracking
- Sulphur embrittlement
- Hydrogen embrittlement

THANK YOU FOR YOUR ATTENTION

Inside copper corrosion

In TR-10-46 section 2.5.2 it is concluded that all corrosion processes inside the canister are considered negligible, based on theoretical assumptions. The possibility of corrosion induced by a condensate with nitric acid and free-radicals which should be expected to precipitate on the coldest spots, i.e. on the copper surface, is neglected.

Worst Case: Ground water ingress at the bottom of a deposition hole creating a cold spot at the FSW. If most of the corrosion takes place in the condensate at the bottom, it could consume up to 4.2 kg of copper based on the amount of available water, i.e. 600g.



(A more common case would be that some area at the inside of the copper tube is the coldest spot, due to the innefective heat transfer in the slot between incert/tube)

Ideal state in the buffer?

The calculations are based on diffusion through 35 cm bentonite in an fully saturated and pressurized ”ideal state”. How many deposition holes is expected to reach this ideal state and after how long time?

Bentonite properties are known to be affected by extensive drying or exposure to highly saline waters (TR-09-29 page 228). Both these problems are expected at the Forsmark site.

Salt precipitates in the deposition hole as the groundwater evaporates and condensates in the tunnel. This creates a brittle compound of crystalline salt mixed with bentonite particles.

Eventually, when the deposition hole starts to get flooded, an partial and assymetric and reduced swelling is expected to create cracks in the altered bentonite.

Microbs can colonise the buffer since it is cracked and not fully pressurised.

TR-11-01, section 10.3.8: “ However, no performance is needed from the buffer as long as the deposition hole is unsaturated, since no mass-transfer between the canister and the groundwater in the rock can take place in the unsaturated stage.” This is not valid for a repository site like Forsmark with atmospheric corrosion by gaseous transport during several hundreds of years.

The atmospheric corrosion will have, after 100 years, created a centimetre-thick cracked and delaminated corrosion product on the whole canister surface (oxides, sulfides and nitrates) which additionally gives new fast path for both gaseous and aqaeous mass-transport.